

# PATENT SPECIFICATION

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## (54) GRAFT COPOLYMER AND PROCESS FOR PRODUCING THE SAME

(71) We, ASAHI-DOW LIMITED, a corporation organized under the laws of Japan, of 1-2 Yurakucho 1-chome, Chiyoda-ku, Tokyo, Japan, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to a graft copolymer comprising polyphenylene ether having styrene polymer segments, formed by continuous polymerization within a short time while melting and kneading a composition for graft polymerization, and to a process for producing the same.

5 Polyphenylene ether resins are engineering plastics having excellent thermal properties, mechanical properties, and electrical properties, that cannot be obtained from conventional thermoplastic plastics, and, consequently, they have extensive fields of use.

10 The superb thermal properties of the polyphenylene ether resin are due to the glass-transition point being far higher than that of any conventional thermoplastic resin; furthermore, the mechanical properties are also excellent because there is no substantial change in physical properties over a wide temperature range. However, a resin comprising polyphenylene ether as the main ingredient has a serious inherent defect that the moldability is inferior to that of conventional thermoplastic resins, 15 due to the high glass transition temperature. A wider field of industrial use is available, if the moldability can be improved without deteriorating the above excellent properties.

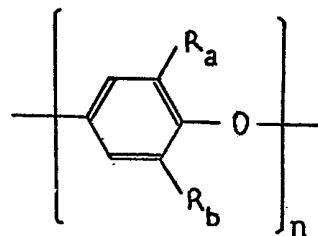
20 A great many modified polyphenylene ethers improved in moldability have been proposed, for instance, ungrafted blends produced by mixing with polystyrene (U.S. Patent No. 3,383,435) or mixing with styrene monomer, followed by curing (U.S. Patent No. 3,356,761); products produced by polymerization of styrene in the presence of polyphenylene ether (Japanese Patent Publication No. 22,069—1967), graft polymerization of styrene with polyphenylene ether (Japanese Patent Publication No. 41,383—1971), or employing styrene grafted polyphenylene ether which is substantially free from homopolymer of polyphenylene ether (Laid-Open Japanese Patent No. 51,150—1975 and Izawa U.S. Patent No. 3,929,931).

25 Besides, it is well known that, in some cases, graft copolymers or block copolymers can be produced by melting and kneading two kinds of polymers or one or more polymers and a vinyl compound. However, there have been no processes for 30 producing thermoplastic resins having no such groups as double bonds in the main chain of the polymer, with high graft polymerization yield, without formation of gel-like polymers and, furthermore, without degradation in mechanical strength caused by the presence of low-molecular-weight compounds. Formation of a gel-like polymer has a deleterious influence on moldability as well as on the surface gloss of a 35 molded article. This is undesirable in practice. Furthermore, while a reaction conducted under severe conditions improves the graft polymerization yield, it produces a 40 large amount of lower molecular weight products, degrades mechanical properties, particularly the impact strength of the product, and is prone to produce a gel-like polymer.



The inventors of the present invention introduced a process for preparing graft copolymers having substantially no polyphenylene ether homopolymer (British Patent Specification No. 1,471,558 and Izawa U.S. Patent No. 3,929,930). The graft copolymer produced by this radical reaction has improved moldability while maintaining excellent mechanical strength as compared with conventional mechanical blends of polyphenylene ether and polystyrene resin. It has now been found that melt flow characteristics of the graft copolymer produced by a radical reaction as well as moldability of the composition containing such a graft copolymer are greatly changed by the reaction conditions of said radical reaction. Said changes are also found to be dependent not only on the structure of grafted segments of styrene polymer in the graft copolymer but also on mutual interactions between main chains of polyphenylene ether during graft polymerization. Namely, when styrene monomer or a mixture of styrene monomer with styrene polymer is heated under agitation in the presence of a relatively large amount of a radical initiator, graft polymerization occurs to produce under specific conditions a graft copolymer free from homopolymers of polyphenylene ether. During graft polymerization, however, due to the inherent nature of polyphenylene ethers, polyphenylene ethers are combined to form larger molecules simultaneously with grafting of polystyrene segments onto the backbone of polyphenylene ethers. Presumably, radicals of polyphenylene ethers are thereby formed to form branched polymers until gel-like products are produced after polymerization is continued for a long time. The graft copolymer obtained by such a procedure is deteriorated in moldability.

According to the present invention there is provided a graft copolymer ether having 10 to 110% by weight, based on the polyphenylene ether, styrene polymer segments grafted thereon, said graft copolymer having been formed by melting and kneading continuously in the substantial absence of solvent a mixture of (a) a polyphenylene ether expressed by the general formula:



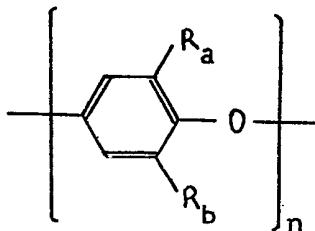
wherein  $R_a$  and  $R_b$  independently represent an alkyl group having 1 to 4 carbon atoms or a halogen atom, and  $n$  represents the degree of polymerization and is 90—250, (b) from 10 to 40% by weight, based on the total of (a) and (b), of a styrene-polymer, preformed or formed in situ, having a weight average molecular weight of at least 100,000 and containing at least 80% by weight of styrene units, and (c) 3 to 30% by weight, based on the total of (a) and (b), of a monomer component containing at least 90% by weight of styrene in the presence of 0.5 to 5% by weight, based on the total of (a) and (b), of a radical initiator at a temperature from 160 to 300°C to complete graft polymerization within a time of from 0.5 to 15 minutes.

The graft copolymer of the present invention has enhanced moldability, better creep characteristics and better surface gloss and transparency as well as color when it is shaped into an article as compared with any one of the copolymer or composition known in the art. While being not bound by any theory, it is believed that mutual interactions between polyphenylene ethers can be disturbed by continuous graft polymerization by melting and kneading a graft composition for a short period. Under such conditions, styrene polymer segments formed in situ and/or from preformed styrene polymer can be grafted onto the backbone of polyphenylene ethers which are not combined to larger molecules, whereby the styrene polymer segments can be grafted onto each of the polyphenylene ether chains. For this purpose, therefore, it is required in one aspect that the graft polymerization time should be short enough to disturb such mutual interactions between polyphenylene ethers. In another aspect, it is also desired that the entire mass of the composition subjected to graft polymerization should be placed under conditions whereby shearing stress may be imposed uniformly throughout said composition.

The present process includes subjecting a styrene polymer to the treatment, while melting and kneading is conducted, in the presence of a radical initiator at high

temperature, and polymerizing a styrene compound in addition thereto. These steps, however, in the past have been considered undesirable from a practical point of view, for the reason that the molecular weight of the styrene polymer would be greatly reduced and the molecular weight of such a polymer produced out of the styrene compound would be quite small. The present process provides an economical process for producing a graft copolymer which is substantially free from polyphenylene ether homopolymer, has no gel-like polymer and has excellent moldability without degradation in properties of the resin, by taking advantage of the types of behaviors mentioned above that have been regarded as undesirable, and by use of a unique combination with polyphenylene ether.

The polyphenylene ether specified in the present invention is expressed by the general formula of



wherein  $R_a$  and  $R_b$ , respectively represent an alkyl group of 1—4 carbon atoms or a halogen atom, e.g., chlorine or bromine, and  $n$  is a number representing the degree of polymerization and ranges from 90 to 250. Examples of such polyphenylene ethers include poly - (2,6 - dimethylphenylene - 1,4 - ether), poly - (2,6 - diethylphenylene - 1,4 - ether), poly - (2 - methyl - 6 - n - butylphenylene - 1,4 - ether), poly - (2 - methyl - 6 - bromophenylene - 1,4 - ether), poly - (2 - methyl - 6 - chlorophenylene - 1,4 - ether), poly - (2 - methyl - 6 - ethylphenylene - 1,4 - ether), poly - (2,6 - dichlorophenylene - 1,4 - ether), and poly - (2,6 - di - n - propylphenylene - 1,4 - ether). Furthermore, it goes without saying that any polyphenylene ether copolymer constituted principally by the chemical structure of the above-mentioned general formula can likewise be usable. A few examples are a copolymer of 2,6-di-substituted phenol with 2,4-di-substituted phenol, a copolymer of 2,6-di-substituted phenol with 2,3,6-tri-substituted phenol, and a copolymer of 2,6-dimethyl phenol with 2-substituted, 3-substituted or 4-substituted phenol. The copolymers should contain over 50% of units made from 2,6-disubstituted phenols, with the balance being from the copolymerizable material. As copolymerizing materials, there can be employed 2,4-dialkyl phenol, e.g., 2,4-dimethyl phenol, 2-alkyl phenol, e.g., 2-methyl phenol, 3-alkyl phenol, e.g., 3-methyl phenol, 4-alkyl phenol, e.g., 4-methyl phenol, 2,3,6-trialkyl phenol, e.g., 2,3,6-trimethyl phenol.

The number-average degree of polymerization,  $n$ , of the polyphenylene ether to be employed for the present process is in the range of 90—250, preferably 100—200. When  $n$  is less than 90, a polyphenylene ether homopolymer is liable to be formed; when  $n$  is more than 250, a gel-like polymer is produced. These products where  $n$  is outside the range stated fail to improve moldability of the product, one of the objects of the present invention, or act to degrade the surface gloss of a molded article.

The relation between the number-average molecular weight  $\bar{M}_n$  and  $[\eta]$  has been discussed in detail when the polyphenylene ether is poly - 2,6 - dimethylphenylene - 1,4 - ether. It is expressed in the following formula:

$$[\eta] = 1.47 \times 10^{-4} \bar{M}_n^{0.85}$$

wherein  $[\eta]$  is the intrinsic viscosity at 30°C in a chloroform solution.

In this case, the molecular weight of the repeating unit of the polymer is 120, the number-average degree of polymerization  $n$  can be calculated easily on the basis of  $[\eta]$ . In the examples hereinafter described, the value of  $[\eta]$  is referred to.

It is desirable that the polyphenylene ether to be employed for the present process be in the form of particles of 2 mm or less in weight-average particle diameter.

The styrene polymer in the present invention is polystyrene or copolymer of styrene and a copolymerizable ethylenically unsaturated compound, e.g., vinyl compound, the amount of the vinyl compound being 20 weight % or less, preferably 10 weight % or less. The copolymers include, for example, styrene-acrylonitrile co-

polymer, rubber-modified polystyrene, styrene-methyl methacrylate copolymer, styrene- $\alpha$ -methylstyrene copolymer, styrene-chlorostyrene copolymer, styrene-maleic anhydride copolymer, styrene-methyl methacrylate-acrylonitrile terpolymer, and copolymers of styrene and one or more of any other copolymerizable compounds having ethylenic unsaturation.

5 There can be employed either preformed styrene polymer or the styrene polymer can be formed in situ while using the free radical catalyst for grafting purposes. It is preferred to use a preformed styrene polymer as specified below.

10 When a preformed styrene polymer is used, the weight-average molecular weight of the preformed styrene polymer is at least 100,000, preferably 120,000 or over, e.g., up to 200,000 or more. When styrene polymer is used where an amount of the vinyl compound or other ethylenically unsaturated compound copolymerizable with styrene is in excess of 20 weight %, the polymer radical which is produced from the styrene polymer is not able to be subjected to graft polymerization on polyphenylene ether in an effective manner under the present conditions. This results only in producing 15 a graft copolymer of polyphenylene ether homopolymer together with a large amount of low molecular weight styrene polymer. Such a product has poor moldability and is inferior in impact strength, and is outside the present invention. The amount of the preformed styrene polymer is in the range of 40—10 weight % based on the total 20 amount of the styrene polymer and polyphenylene ether. When the amount of the styrene polymer is less than 10 weight %, the polyphenylene ether homopolymer is left as a residue, which adversely influences moldability. When the amount of the styrene polymer is in excess of 40 weight %, the graft copolymer obtained is prone to deteriorate in mechanical strength, especially impact strength.

25 The styrene containing monomer component specified in the present invention contains 90 to 100 weight % styrene and 10 weight % or less of one more ethylenically unsaturated compounds, e.g., vinyl compounds capable of being subjected to radical copolymerization. Examples of the said radical polymerizable ethylenically unsaturated compounds are acrylonitrile, methyl methacrylate  $\alpha$ -methylstyrene, chlorostyrene, vinyltoluene, e.g., p-vinyl toluene and maleic anhydride.

30 The amount of the monomeric styrene-containing composition is in the range of 3—30 parts by weight, preferably 5—20 parts by weight, for every 100 parts by weight of resin consisting of 60—90 weight % of polyphenylene ether and 40—10 weight % of preformed styrene polymer. When the amount of the monomeric styrene 35 composition is less than 3 parts by weight, the effect of the present invention cannot be achieved. On the other hand, the graft copolymer obtained by the present process is prone to be deteriorated in mechanical strength, especially impact strength, when the amount exceeds 30 parts. The percentage ratio of grafted styrene polymer based on polyphenylene ether is from 10 to 110% by weight.

40 A radical initiator is indispensable for the present invention, in order to promote graft reaction onto the polyphenylene ether. Examples of compounds capable of being employed as the radical initiator are di-t-butyl peroxide, t-butyl cumyl peroxide di-cumyl peroxide, 2,5 - dimethyl - 2,5 - di(t - butylperoxy) hexyne - 3, 2,5 - dimethyl-2,5 - di(t - butylperoxy)hexane, t - butyl hydroperoxide, cumene hydroperoxide, 45 paramethanehydroperoxide, 2,5 - dimethylhexa - 2,5 - di - hydroperoxide, acetyl peroxide, octanoyl peroxide, 3,5,5 - trimethyl hexanoyl peroxide, benzoyl peroxide, p - chlorobenzoyl peroxide and  $\alpha,\alpha'$  - bis (t - butylperoxy) para - di - isopropylbenzene. The above-mentioned initiators are merely illustrative and other free radical initiators can be employed.

50 The radical initiator can also be employed in the form of a combination of two or more kinds of radical initiators, e.g., in association with a change in polymerization temperature. In the process of the present invention as mentioned above wherein 3—30 parts by weight of a styrene-containing monomer component is added for every 100 parts by weight of a mixed resin of polyphenylene ether and styrene polymer, the amount of the radical initiator is in the range of 0.5—5 parts by weight, preferably 55 0.8—4 parts by weight per 100 parts by weight of mixed resin, when the amount of the initiator is less than 0.5 part by weight, the graft reaction proceeds insufficiently; while with more than 5 parts by weight, a gel-like polymer is easily produced.

60 The process of the present invention is conducted in the substantial absence of a solvent. When a solvent is present, there is produced a large amount of low molecular weight polymer from the styrene polymer used in the present invention, which low molecular weight polymer does not play a role in graft reaction, in association with the fact that the reaction is conducted at a higher temperature than employed in the conventional technology. Furthermore, polymers produced from the

monomer component are low in graft efficiency, accompanying low molecular weight polymers which are present in a large amount. As a result, the properties of the polymer thus obtained are impaired, especially the impact strength thereof. This is not desirable. However, the solvent may be used in an amount of approximately 3 weight % based on a combination of the styrene polymer and polyphenylene ether in order to make it possible to use the initiator in the form of a solution.

It is critical in the present invention to complete graft polymerization within a short period in the range from 0.5 to 15 minutes, preferably from 0.7 to 10 minutes. The reaction time is expressed in terms of residence time (minute) which is determined by the ratio of the volume V (liter) of the composition to be graft polymerized present in a reactor to the out-put volume of the product per unit time Q (liter/minute). When the residence time is less than 0.5 minutes, homopolymers of polyphenylene ether remain in the product and unaltered styrene monomers are also left to require steps for removal of monomers whereby the process is rendered more complicated. On the other hand, when the residence time is over 15 minutes, gel-like polymers are prone to be formed to deteriorate moldability of the graft copolymer obtained. The value V is generally in the range from 0.3 to 300 liters, while the value Q falls within the range from 0.05 to 20 liter/minute, in a presently available apparatus.

The temperature for conducting the present process is in the range of 160—300°C, preferably 200—300°C. A temperature below 160°C causes the polyphenylene ether homopolymer to be left in the form of a residue and to have ethylenically unsaturated compound such as styrene left as a residue in the form of unaltered monomer, particularly when a high level of productivity is desired with short reaction time. On the other hand, a temperature in excess of 300°C promotes the production of gel-like polymer which impairs moldability of the graft copolymer for molding.

The composition to be graft polymerized in the present invention should preferably be placed under uniform mechanical shearing stress during polymerization. Such a uniform shearing stress is found to be attained when the composition is permitted to pass through a zone of which the length perpendicular to the surface strain for imposing shearing stress is as small as 1 to 50 mm, preferably 3 to 30 mm. While the composition is passed through such a narrow space, shearing stress is imposed at shear rate of at least 10 sec<sup>-1</sup>. A shear rate of less than 10 sec<sup>-1</sup> may sometimes cause formation of polyphenylene ether homopolymer or a gel-like polymer. The upper limit on the shear rate is not critical. Thus, it can be as much as 300 sec<sup>-1</sup>.

A typical method for imparting uniform shearing stress is to melt and knead the composition to be grafted by extrusion, preferably through a screw type extruder. Either a monoaxial or biaxial (rotating in the same or opposite directions) type screw extruder may be available. A further improved extruder, for example, co-kneader can also be used. The diameters of screw in such an extruder cannot be determined in general terms but they are dependent on the shapes of screws. For example, the diameter is selected in the range from 30 m/m to 500 m/m, preferably from 50 m/m to 200 m/m.

The ratio of length by diameter (L/D) of screw is selected in the range from 5 to 50. The revolution rate is selected in the range from

$$\frac{5}{60} \text{ to } \frac{400}{60} \text{ r.p.s., preferably from } \frac{30}{60} \text{ to } \frac{300}{60} \text{ r.p.s.}$$

Any other polymers, glass fibers, carbon fibers, carbon black, fillers, such as silica, plasticizer, fire retardant or the like, may be added, so long as they do not inhibit the graft copolymerization reaction. For the purpose of improving impact resistance, it is especially desirable to add a rubber-like polymer. The only thing required for the rubber-like polymer is that the modulus of elasticity of the polymer is less than that of the graft copolymer to be obtained by the present process. Examples of such rubber-like polymers are polybutadiene, butadiene-styrene copolymer, (and other conjugated diene rubbers such as polyisoprene), polyethylene, polypropylene, ethylene copolymers, e.g. ethylene-amyrene copolymer, ethylene-propylene copolymers, polyisobutylene, polyacrylic acid ester, e.g., 2-ethylhexyl acrylate polymer, polyamides (for example, 6-nylon and 6,6-nylon), polyesters (for example, polyethylene terephthalate), and any modified polymers of the above. The amount of the rubber-like polymer to be added is such as is generally known in connection with the rubber-like

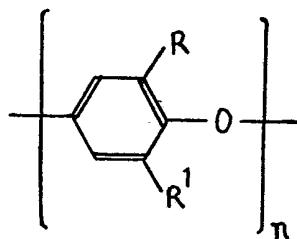
polymer-reinforced resin compositions, and is preferably 1—30 parts by weight for every 100 parts by weight of the resin comprising polyphenylene ether and styrene polymer.

The graft copolymer obtained by the present invention contains no polyphenylene ether homopolymer, which is confirmed by analyzing the copolymer according to the method reported by A. Factor (J. Polymer Science, 7B, 205 (1969)), that is polyphenylene ether forms a complex with methylene chloride and the complex is insoluble in methylene chloride. The complex, when subjected to heating, easily evolves methylene chloride, to obtain polyphenylene ether as the residue. This is confirmed by the fact that, when the polymer obtained by the present process is dissolved in methylene chloride to form a uniform solution no precipitate is produced, or that, when some precipitate is produced after the solution is allowed to stand for many hours and the precipitate is thoroughly washed and dried, the polymer thus obtained contains inseparable polystyrene or a styrene copolymer. One skilled in the art could confirm the presence of polyphenylene homopolymer by A. Factor's process, if there were 10 parts by weight or more of residual polyphenylene ether homopolymer in a polymer obtained by the present process. Furthermore, the fact that the graft copolymer obtained by the present invention has no polyphenylene ether homopolymer can likewise be confirmed by a composition fractionating process wherein a special combination of a solvent and a non-solvent is employed for polyphenylene ether and polystyrene. In order to carry out such a process a polymer containing polyphenylene ether and polystyrene is dissolved in benzene, n-heptane is added and proper fractionation is effected in a careful manner.

The graft copolymer obtained by the present invention, when subjected to the fractionation of the composition, has inseparable polystyrene contained even in 5 weight % or less of the fractionated polymer. Shown in the Figure is the result of the fractionation of the graft copolymer obtained by the present invention, together with the result using a mixed resin of polyphenylene ether and polystyrene taken as a comparison example.

The graft copolymer obtained by the process of the present invention, containing no polyphenylene ether homopolymer, can be employed by itself but it can also be blended with other polymers as well. Concrete examples of such other polymers are styrene polymers such as styrene-acrylonitrile copolymer or styrene-methyl methacrylate copolymer, and rubber modified polystyrene, butadiene rubber modified styrene-acrylonitrile copolymer (ABS terpolymer), acrylic rubber modified polystyrene, acrylic rubber modified styrene-acrylonitrile copolymer, ethylene-propylene copolymer modified polystyrene, and ethylene-methyl methacrylate copolymer modified polystyrene. Our pending application No. 4906/77 (Serial No. 1 571 015) is connected with a thermoplastic resin comprising:

(I) a graft copolymer having an ethylenically unsaturated aromatic compound polymer, or a copolymer of said compound and not more than 30mol%, based on the copolymer, of a copolymerizable compound grafted onto a polyphenylene ether of the formula:



wherein, R and R<sup>1</sup> each denote a hydrogen atom or an alkyl group having one to four carbon atoms and n is the degree of polymerization, the graft copolymer containing substantially no homopolymer of polyphenylene ether; and

(II) a graft copolymer having an ethylenically unsaturated aromatic compound polymer, or a copolymer of said compound and not more than 30mol%, based on the copolymer, of a copolymerizable compound grafted onto a copolymer of ethylene with 1.0 to 40 mol percent of at least one unsaturated compound of the formula  $\text{CH}_2=\text{CH}-\text{OCOR}_1$  or  $\text{CH}_2=\text{CR}_2-\text{COOR}_3$ , wherein R<sub>1</sub> denotes an alkyl group having one to four carbon atoms and each of R<sub>2</sub> and R<sub>3</sub> a hydrogen atom or an alkyl group having one to four carbon atoms, the amount of said polyphenylene ether

being from 20 to 85% by weight and that of said copolymer of ethylene being from 3 to 40% by weight based on the total composition, the composition as a whole containing substantially no homopolymer of polyphenylene ether.

5 Furthermore, as indicated above the present resins can further be modified by adding thereto glass fiber, carbon fibers, carbon black, fillers such as silica, various polymers, plasticizers and/or fire retardants.

10 The single Figure of the accompanying drawing is a graph which shows fractional compositions of the reaction product obtained in Example 3 and resin composition obtained in Comparative Example 2, by fractionation with benzene/n-heptane.

15 The following examples explain the present process in detail but are not intended to limit the scope of the invention thereto. All "parts" and "%" represent parts by weight and % by weight, respectively.

10 In the Examples, physical properties are measured by the following methods:

15	Izod impact strength	ASTM—D—256	15
	Melt index	ASTM—D—1238	
		(except for the temperature of 250°C under load of 10 kg)	
	Heat distortion temperature	ASTM—D—648	
	Surface gloss	ASTM—D—523	

20 Examples 1 to 3; Comparative Examples 1 and 2.

20 700 g of poly(2,6-dimethyl phenylene-1,4-ether) with average particle diameter of 0.1 mm having a  $[\eta]$  of 0.58 dl/g and 300 g of polystyrene (manufactured by Asahi-Dow Ltd., under the trade name of Styron 690 — "Styron" is a Registered Trade Mark) were subjected to dry blending by the employment of a Henschel mixer at the low rate thereof. While thus blending at this low rate, a uniform solution of 20 g of di-t-butyl peroxide in 200 g of styrene was added little by little. The mixture was subjected to agitation for 5 minutes at a high rate. A graft reaction was carried out under melting and kneading at 260°C, in a monoaxial extruder provided with a 40 mm diameter vent, applying various shear rates by changing the speed of revolution of the screw of the extruder. The depth of screw channel in metering zone was 2 mm and the total inner volume was 0.5 liter.

25 The thus prepared reaction product (2.0 g) was dissolved in 40 ml of methylene chloride and the solution was left for 3 hours. When precipitates were formed, the precipitates were filtered and washed with methylene chloride and then with methanol, followed by drying at 120°C under reduced pressure for 2 hours to obtain a polymer. Then, the polystyrene content in this polymer was determined by infra-red absorption spectrum analysis (by the same method hereinafter). The results are shown in Table 1 in relation with shear rate.

30 The shear rate was calculated from the following equation at the metering zone of the extruder wherein the graft polymerization occurs:

$$S = \frac{\pi DN}{h}$$

35 wherein S is shear rate ( $\text{sec}^{-1}$ ), D screw diameter (mm), N revolution rate of screw (r.p.s.) and h depth of screw channel (mm).

TABLE 1

	Shear rate (Sec <sup>-1</sup> )	Precipitation rate (%)	Polystyrene content (%)	Reaction time (min.)
Comparative Example 1	5	43	3	22
Example 1	15	5	12	13
Example 2	87	2	14	2.2
Example 3	123	0	—	1.5

Precipitation rate is desirably 15% or less for the purpose of remarkable improvement of moldability which is the effect of the present invention. Further, polystyrene content in the precipitate, which depends also on the precipitation rate, is desired to be 5% or more. As apparently seen from Table 1, it is desirable in the present process to melt and knead the composition while giving at least 10 sec<sup>-1</sup> of shear rate.

The Figure shows the result of subjecting the reaction product obtained in Comparative Example 1 to the fractionation of the composition by the employment of benzene-n-heptane (fraction nos. shown as . . . 5,6, . . .). Comparative Example 2 is also shown in the Figure (fractions nos. shown as . . . 5',6', . . .). Comparative Example 2 was conducted in such a manner that 700 g of the same polyphenylene ether and 300 g of the same polystyrene as used in Example 3 were blended together twice at 260°C in a monoaxial extruder provided with a 40 mm diameter vent. It is clear from the Figure that the graft copolymer obtained by the present invention as referred to in Example 3 is a copolymer having the characteristic compositional distribution of polyphenylene ether and polystyrene, and is free from polyphenylene ether homopolymer. It is also clear that no graft copolymer is contained in the composition obtained by mere blending through an extruder.

Furthermore, the moldability of the reaction products obtained in Examples 1 to 3 was subjected to evaluation, and the series of results obtained are shown in Table 2.

TABLE 2

	Moldability (MI) (g/10 min)
Comparative Example 1	7
Example 1	22
Example 2	21
Example 3	24

It is clear from the Table 2 that the reaction product obtained by the present invention has excellent moldability.

## Example 4.

700 g of poly(2,6-dimethyl phenylene-1,4-ether) having a  $[\eta]$  of 0.48 dl/g and 0.5 mm average particle diameter and 300 g of the same polystyrene as employed in Example 1 were subjected to dry blending by the employment of a blender. To this

5 mixture was added a solution of 30 g of 2,5-dimethyl-2,5-di(t-butyl peroxy)hexane in 200 g of styrene, and the product thus obtained was further subjected to mixing. The mixture was then subjected to a graft reaction under melting and kneading at the temperature of 250°C, by the employment of a biaxial extruder (rotating in opposite directions) provided with a 30 mm diameter vent, applying a shear rate of 95 sec<sup>-1</sup>. The depth of screw channel h in the metering zone of the extruder was 5 mm, the total inner volume 0.4 liter and the out-put volume at the rate of 0.12 liter/minute. The reaction time, that is, the residence time in the extruder, was as short as 4 minutes. Despite this, virtually no unaltered styrene was volatilized through the vent of the extruder. Thus substantially all of the amount was subjected to the polymerization reaction.

10 The reaction product obtained contained 59% of polyphenylene ether and the ratio of grafted polystyrene was 52% based on polyphenylene ether. The composition of the reaction product was analyzed by infra-red absorption spectrum after the 10 product was dried at 215°C under reduced pressure in a drier for one hour. The ratio of grafted styrene was determined by dissolving homogeneously 2 g of the sample 15 polymer of the product in 10 ml of chloroform, followed by careful addition of 100 ml of methyl ethyl ketone thereby to precipitate graft copolymer. The precipitate was recovered by filtration and dried at 215°C under reduced pressure in a drier for one 20 hour. The resulting polymer was weighed and subjected to infra-red absorption 25 spectrum analysis. From the results of measurements, the ratio of grafted styrene was calculated.

25 2.0 g of the reaction product thus obtained was dissolved in 40 ml of methylene chloride and left to stand for 6 hours. No precipitate was obtained.

25 1,000 g of the reaction product and 150 g of polybutadiene rubber modified 25 polystyrene containing 40% of butadiene were blended with each other, and subjected further to polymer blending by the employment of an extruder, whereby a resin compound was obtained.

30 Comparative Example 3.  
30 As comparative Example 3, the polyphenylene ether, the polystyrene, and the 30 polybutadiene rubber modified polystyrene employed in Example 4 were subjected to blending in such a manner as to obtain the same resin composition as above. The composition thus obtained was subjected twice to polymer blending by the employment of an extruder, whereby a resin composition was obtained. These resin compositions 35 thus obtained were subjected to evaluation in terms of moldability, heat distortion temperature, the surface gloss of molded pieces, and molding anisotropy of molded articles, respectively. The anisotropy of the injection molded article was expressed in terms of Izod impact strengths of two samples cut parallel (//) and perpendicular (⊥) to the direction of injection from the injection molded article shaped in flat 40 plates 9 cm in diameter and 3 mm in thickness. The results are shown in Table 3.

TABLE 3

	Example 4	Comparative Example 3
Moldability (g./10 min.)	18.0	5.1
Heat distortion temperature (°C)	141.0	143.0
Surface gloss	81.0	57.0
Impact strength (Kg.cm./cm)	(//) 19 (⊥) 18	25 14

It is clear from Example 4 that a molding material is produced according to the present process which has excellent moldability and can provide molded articles having excellent surface gloss and anisotropy while keeping mechanical and thermal properties.

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Furthermore, it is clear that, when compared with the conventional technology, for instance, the process described in British Specification No. 1,471,558 and Izawa U.S. Patent No. 3,929,930, the present process is a simplified one requiring no steps for removal of a solvent, and results in a higher yield in a shorter time in the presence of a larger amount of initiator and at a higher temperature than for conventional radical polymerization although substantially no solvent but styrene is present.

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Example 4 was repeated except for the use of poly(2,6-dimethyl phenylene-1,4-ether) with average particle diameter of 1.1 mm having intrinsic viscosity of 0.65 dl/g and as polystyrene Styron 683: (produced by Asahi-Dow Limited, Japan).

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The reaction product (2.0 g) was dissolved in 40 ml of methylene chloride, and left to stand for 3 hours whereby no precipitate was formed. This product had a melt index of 19 g/10 min.

Example 6.

8,000 Grams of poly(2,6-dimethylphenylene-1,4-ether) with average particle diameter of 2.0 mm having intrinsic viscosity of 0.45 dl/g and 2,000 g of polystyrene (Styron 666, produced by Asahi-Dow Limited, Japan) were dry blended in a Henschel mixer. Separately, a solution having 150 g of di-tert.-butyl peroxide dissolved in 2,000 g of styrene was prepared and 1/5 of this solution was added into the Henschel mixer and stirred for 7 minutes. This operation was repeated 5 times, followed by further stirring for 20 minutes. The resulting mixture was fed to 50 mm $\phi$  biaxial extruder (h=8 mm, V=2.0 l, Q=1.1 litre/min; rotating in the same direction) equipped with a vent and melted and kneaded at 260°C while giving a shear rate of 105 sec $^{-1}$  thereby to conduct graft polymerization. The residence time was 2.0 minutes.

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Two grams of the resulting reaction product were dissolved in 40 ml of methylene chloride and the solution was left to stand for 3 hours, whereby 3% of precipitates were formed. The precipitates formed contained 11% of polystyrene. The reaction product had 67% of polyphenylene ether and 33% of grafted polystyrene.

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A mixture comprising 1,000 g of the reaction product, 150 g of rubber-reinforced polystyrene (Styron 475, produced by Asahi-Dow Limited, Japan) and 150 g of the polybutadiene-modified polystyrene as used in Example 4 was blended through an extruder to obtain a resinous composition. The resinous composition was tested for moldability and impact strength. As the result, it had a melt index of 20 g/10 min. and Izod impact strength in the parallel direction of 18 Kg · cm/cm and in the perpendicular direction of 17 Kg · cm/cm.

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Comparative Example 4.

Into an autoclave of 10 litre capacity was charged a mixture of 3.0 kg of the same poly(2,6-dimethylphenylene-1,4-ether) as used in Example 6, 0.75 kg of styrene and 120 g of di-tert.-butyl peroxide and the mixture was dissolved homogeneously at 120°C. While the inner temperature of the autoclave is maintained at 140—145°C, graft polymerization was conducted for two hours. The product was dried at 215°C under reduced pressure in a drier for two hours to remove unaltered styrene to obtain a graft copolymer. This copolymer contained 86% of polyphenylene ether and had a melt index of 4 g/10 min. A solution of 2.0 g of this copolymer in 40 ml of methylene chloride was left to stand for three hours, whereby there was formed no precipitate.

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This copolymer was blended similarly as in Example 6 with the same polystyrene and polybutadiene-modified polystyrene as used in Example 6 to obtain a resinous composition.

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This composition had a melt index of 5.5 g/10 min., Izod impact strength in the parallel direction of 6.5 Kg · cm/cm and in the perpendicular direction of 4.0 Kg · cm/cm, being by far lower in moldability and mechanical strength than the composition of this invention.

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Comparative Example 5.

Example 4 was repeated except that cumene hydroperoxide and polyphenylene ether having intrinsic viscosity of 0.34 dl/g were used. A solution of 2.0 g of the reaction product in 40 ml of methylene chloride was left to stand for 3 hours, whereby 26% of precipitate was formed. Said precipitate contained 1% of polystyrene.

## Examples 7 and 8; Comparative Example 6.

A graft reaction was conducted in the same manner as Example 4, except that the amount of the radical initiator was modified. The amounts of the radical initiator and the results thus obtained are as shown in Table 4.

TABLE 4

	Radical initiator (g)	Precipi-tation rate (%)	Poly-styrene content (%)	Styrene* con-versation (%)	Ratio of grafted poly-styrene (%)
Example 7	7	9	13	95	57
Example 8	40	0	—	97	77
Comparative Example 6	3	36	2	80	9

\*) Styrene conversion was determined by infra-red absorption spectrum of the polymer obtained after drying the reaction product at 215°C under reduced pressure in a drier for one hour.

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It is clear that the amount of radical initiator is critical for accelerating graft reaction and complete substantially polymerization thereby to eliminate the step for removal of unaltered monomers, even if the other conditions are satisfied, for the present process to be successful.

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Moldability of the reaction product obtained in Comparative Example 6 was 2.4 g/10 min. as shown by melt index, which was considerably inferior to moldability of copolymer obtained by the method of the present invention.

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## Examples 9 and 10.

A graft reaction was effected in the same manner as Example 4, except that the kinds of the radical initiator were varied. The radical initiator employed and the results are shown in Table 5.

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TABLE 5

	Radical initiator	Precipitation rate (%)	Polystyrene content (%)
Example 9	Cumene-hydroperoxide	8	7
Example 10	Di-t-butyl-di-peroxyphthalate	3	13

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## Examples 11 and 12; Comparative Example 7.

A graft reaction was carried out in the same manner as Example 4, except that the amount of styrene was varied. The results thus obtained are shown in Table 6.

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The amounts of styrene (parts by weight) are shown for every 100 parts by weight of the total amount of poly(2,6-dimethyl phenylene-1,4-ether) and polystyrene.

TABLE 6

	Amount of styrene (Part by weight)	Precipitation rate (%)	Poly-styrene content (%)	Ratio of grafted polystyrene (%)
Example 11	5	9	12	31
Example 12	10	6	14	37
Example 4	20	0	—	52
Comparative Example 7	35	0	—	—

Impact strength of the resin composition obtained by subjecting the reaction product obtained in Comparative Example 7 to polymer blending in the same manner as Example 4 was evaluated and found to be 7.2 Kg · cm/cm (//) and 6.5 Kg · cm/cm (⊥), which values are quite low.

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## Examples 13 to 15.

A graft reaction was conducted in the same manner as Example 2, except that the amounts of poly(2,6-dimethyl phenylene-1,4-ether) and polystyrene and also the temperature were modified. The percentage composition and the results are shown in Table 7.

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TABLE 7

	Poly(2,6-di-methyl phenylene-1,4-ether) (%)	Poly-styrene (%)	Tempera-ture (°C)	Precipi-tation rate (%)	Poly-styrene content (%)
Example 13	85	15	290	8	8
Example 2	70	30	260	2	14
Example 14	65	35	260	0	—
Example 15	65	35	220	4	15

## Comparative Example 8.

Example 9 was repeated except that 280 g of styrene was used, the temperature of the extruder was changed to 150°C and the residence time was changed to 11 minutes by changing the amount of feed. As the result, 20 g of unaltered styrene was evaporated at the vent portion and 92 g of unaltered styrene remained in the reaction product. The reaction product contained unaltered styrene was dried at 215°C under reduced pressure in a drier for one hour to obtain 1,163 g of a polymer.

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A solution of 2.0 g of the polymer in 40 ml of methylene chloride was left to stand for 3 hours, whereby 40% of precipitate was formed. The precipitate contained 2% of polystyrene.

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## Examples 16 to 18.

Example 1 was repeated except that the revolution rate and the amount of feeding were varied to change the shear rate and the residence time to obtain the results as shown in Table 8.

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TABLE 8

	Shear rate (sec <sup>-1</sup> )	Residence time (min.)	Precipitation rate (%)	Poly-styrene content (%)	Styrene conversion (%)	Ratio of grafted poly-styrene (%)
Example 16	175	1.1	0	—	95	53
Example 17	230	0.9	3	12	95	52
Example 18	300	0.7	5	10	90	45

## Comparative Example 9.

Example 4 was repeated, changing the residence time to 0.3 minutes by controlling the revolution rate of screw in the extruder. During graft polymerization, unaltered styrene was evaporated, showing clearly that the polymerization of styrene was incomplete. A part of the reaction product was dried at 215°C under reduced pressure in a drier for one hour. A sample of this product was measured for its composition by infra-red absorption spectrum and the content of unaltered styrene was calculated from the result to be 32%. A solution of 2.0 g of this product in 40 ml of methylene chloride was left to stand for 3 hours, whereby 46% precipitate was formed. The precipitate contained less than 2% of polystyrene.

## Example 19.

Using an industrial scale biaxial extruder provided with a vent (rotating in opposite directions) having 120 mm diameter, graft reaction was practised according to the same procedure as in Example 4 except that the mixture was melted and kneaded at 270°C under shear rate of 135 sec<sup>-1</sup>. The depth of screw channel in metering zone of the extruder was h=15 mm, the total volume V=26 liter and the rate of output volume Q=12 liter/min., thus giving a residence time of 2.5 minutes. Substantially no unaltered styrene was evaporated from the vent portion of the extruder and conversion of styrene was measured to be 98%. A solution of 2.0 g of the reaction product in 40 ml of methylene chloride was left to stand for 6 hours, whereby no precipitate was formed.

By use of the reaction product obtained, the same composition as in Example 4 was prepared in the same manner. The composition obtained had a melt index of 20.5 g/10 min., a heat distortion temperature of 140°C, surface gloss of 83.0, Izod impact strength in the parallel direction of 20 Kg · cm/cm and in the perpendicular direction of 19 Kg · cm/cm. This shows that excellent compositions not known in the art can be produced from the graft copolymer produced by means of a commercial apparatus.

## Example 20.

Example 4 was repeated using a polyphenylene ether having a  $[\eta]$  of 0.51 dl/g and 1.2 mm average particle diameter obtained by subjecting 80 parts of 2,6-xylenol and 20 parts of 2,4-xylenol to polymerization in the presence of bis(acetylacetone) ethylene-di-imine copper, nickel chloride hexahydrate and pyridine, as a catalyst.

When 2.0 g of the reaction product thus obtained was dissolved in 40 ml of methylene chloride and left to stand for 3 hours, no precipitate was produced. However, after a lapse of 6 hours, 7.5% was found to have been precipitated.

This precipitate had 11% of polystyrene.

## Example 21.

Example 4 was repeated using a polyphenylene ether having a  $[\eta]$  of 0.50 dl/g and 0.8 mm average particle diameter, obtained by subjecting 72 parts of 2,6-dimethylphenol and 28 parts of 2,3,6-trimethylphenol to copolymerization in the

presence of cuprous iodide and n-butyl-amine as a catalyst.

2.0 g of the reaction product thus obtained was dissolved in 40 ml of methylene chloride and left to stand for 3 hours to produce 3% of a precipitate which had 12% of polystyrene.

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Example 22.

700 g of poly(2,6-dimethyl phenylene-1,4-ether) having a  $[\eta]$  of 0.52 dl/g and 0.3 mm average particle diameter, 300 g of styrene-methyl methacrylate copolymer containing 6% of methyl methacrylate, 40 g of di-tert.-butyl peroxide and 150 g of styrene were mixed. Graft reaction was conducted under melting and kneading at 270°C under a shear rate of 111 sec<sup>-1</sup> for a residence time of 1.7 minutes, by the employment of an extruder provided with a two-shaft vent of 30 mm diameter.

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2.0 g of the reaction product thus obtained was dissolved in 40 ml of methylene chloride and left to stand for 3 hours. No precipitate was produced.

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Example 23.

Graft reaction was conducted similarly as in Example 4, except 190 g of styrene and 10 g of acrylonitrile were used in place of styrene alone.

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2.0 g of the reaction product thus obtained was dissolved in 40 ml of methylene chloride. After a lapse of 3 hours, a precipitate was formed (4%) which had 13% styrene polymer.

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A resin composition was produced according to Example 4 by use of the reaction product thus obtained, and impact strength was evaluated.

Impact strength in the parallel direction was 16 Kg · cm/cm, and that in the perpendicular direction was 14 Kg · cm/cm.

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Comparative Example 10.

Graft reaction was conducted according to Example 4 using 150 g of styrene and 50 g of acrylonitrile, in place of styrene alone.

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2.0 g of the reaction product thus obtained was dissolved in 40 ml of methylene chloride. After a lapse of 3 hours, 17% thereof was precipitated. The polymer thus obtained had 4% of styrene polymer.

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Impact strength of the resin composition was obtained in the same manner as in Example 4, by the employment of the said reaction product, to find 3.6 Kg : cm/cm (//) and 0.9 Kg · cm/cm (⊥). The composition was not satisfactory for practical use.

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Comparative Example 11.

Into an autoclave of 3 litre capacity were charged 200 g of ethyl benzene, 200 g of styrene, 700 g of the same poly(2,6-dimethylphenylene-1,4-ether) as used in Example 4 and 300 g of polystyrene and the mixture was heated to 120°C to be homogeneously dissolved. The resulting solution was heated gradually up to 220°C over 30 minutes and a solution of 20 g of di-tert.-butyl peroxide in 100 g of ethyl benzene was injected by pressure of nitrogen gas, followed by continued agitation at 220°C for one hour. Then the mixture was cooled and the product was recovered, followed by removal of volatiles by drying at 215°C under reduced pressure for one hour. A solution of 2.0 g of this reaction product in 40 ml of methylene chloride was left to stand for 3 hours, whereby 17% precipitate was formed. The precipitate contained 3% of polystyrene.

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The resinous composition prepared from 800 g of this reaction product and the same polybutadiene-modified polystyrene in the same manner as in Example 4 had Izod impact strength in the parallel direction of 4 Kg · cm/cm and in the perpendicular direction of 3 Kg · cm/cm, showing that said resinous composition cannot practically be used.

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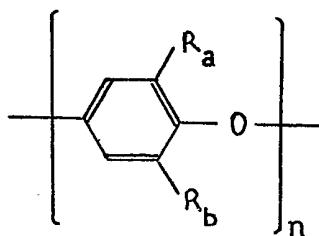
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WHAT WE CLAIM IS:—

1. A graft copolymer polyphenylene ether having 10 to 110% by weight, based on the polyphenylene ether, styrene polymer segments grafted thereon, said graft copolymer having been formed by melting and kneading continuously in the substantial absence of solvent a mixture of (a) a polyphenylene ether expressed by the general formula:

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wherein  $R_a$  and  $R_b$  independently represent an alkyl group having 1 to 4 carbon atoms or a halogen atom, and  $n$  represents the degree of polymerization and is 90—  
 5 250, (b) from 10 to 40% by weight, based on the total of (a) and (b) of a styrene-polymer, preformed or formed in situ, having a weight average molecular weight of at least 100,000 and containing at least 80% by weight of styrene units, and (c) 3 to 10 30% by weight, based on the total of (a) and (b), of a monomer component containing at least 90% by weight of styrene in the presence of 0.5 to 5% by weight, based on the total of (a) and (b), of a radical initiator at a temperature from 160 to 300°C to complete graft polymerization within a time of from 0.5 to 15 minutes.

2. A graft copolymer according to Claim 1 wherein the polyphenylene ether employed is a homopolymer.

3. A graft copolymer according to Claim 1 wherein the polyphenylene ether employed is a copolymer containing over 50% of 2,6-disubstituted phenol units.

4. A graft copolymer according to Claim 3 wherein the units copolymerised with the 2,6-disubstituted phenol units are units from a mono-alkyl phenol, a dialkyl phenol or a trialkyl phenol.

5. A graft copolymer according to any one of Claims 1 to 4 wherein the polyphenylene ether employed is in the form of particles of 2 mm or less in weight-average particle diameter.

20 6. A graft copolymer according to any one of Claims 1 to 5 wherein the 2,6-disubstituted units of the polyphenylene ether are derived from 2,6-dimethyl-1,4-phenylene ether.

25 7. A graft copolymer according to any one of Claims 1 to 6 wherein the styrene polymer is polystyrene.

8. A graft copolymer according to any one of Claims 1 to 6 wherein the styrene polymer is styrene-acrylonitrile copolymer, styrene-methyl methacrylate copolymer, styrene- $\alpha$ -methylstyrene copolymer, styrene-chlorostyrene copolymer, styrene-maleic anhydride copolymer, or styrene-acrylonitrile-methyl methacrylate copolymer.

30 9. A graft copolymer according to any one of Claims 1 to 8 wherein the monomer (c) consists of styrene.

35 10. A graft copolymer according to any one of Claims 1 to 8 wherein the monomer (c) consists of a mixture of styrene and less than 10 weight % of one or two compounds selected from acrylonitrile, methyl methacrylate,  $\alpha$ -methylstyrene, chlorostyrene and maleic anhydride.

11. A graft copolymer according to any one of Claims 1 to 10 wherein the poly-styrene segments are formed while placing the mixture under uniform shearing stress through out said mixture.

40 12. A graft copolymer according to Claim 11 wherein the mixture is permitted to pass through a zone of which the length perpendicular to the surface strain for imposing shearing stress is as small as 1 to 50 mm under shear rate of 10 sec<sup>-1</sup> or over.

13. A graft copolymer according to any one of Claims 1 to 12 wherein the mixture is melted and kneaded by extrusion.

45 14. A graft copolymer according to any one of Claims 1 to 13 wherein 0.8 part to 4 parts by weight of a radical initiator is used per 100 parts by weight of the total of (a) and (b).

15. A graft copolymer according to Claim 1 substantially as described in any one of the Examples.

50 16. A thermoplastic resinous composition comprising a graft copolymer according to any one of Claims 1 to 15.

17. A method of preparing a graft copolymer polyphenylene ether having 10 to 110% by weight, based on the polyphenylene ether, styrene polymer segments grafted thereon, comprising melting and kneading continuously in the substantial absence of solvent a mixture of (a) a polyphenylene ether expressed by the general formula:

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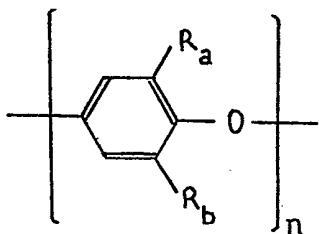
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wherein R<sub>a</sub> and R<sub>b</sub> independently represent an alkyl group having 1 to 4 carbon atoms or a halogen atom, and n represents the degree of polymerization and is 90—250, (b) from 10 to 40% by weight, based on the total of (a) and (b), of a styrene-polymer, preformed or formed in situ, having a weight average molecular weight of at least 100,000 and containing at least 80% by weight of styrene units, and (c) 3 to 30% by weight, based on the total of (a) and (b), of a monomer component containing at least 90% by weight of styrene in the presence of 0.5 to 5% by weight, based on the total of (a) and (b), of a radical initiator at a temperature from 160 to 300°C to complete graft polymerization within a time of from 0.5 to 15 minutes.

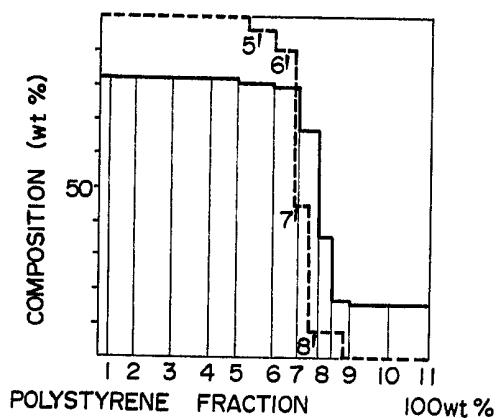
18. A method according to Claim 17 substantially as described herein with reference to the accompanying drawing or in any one of the Examples.

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## POLYPHENYLENE ETHER



— : GRAFT COPOLYMER OBTAINED BY  
THE PRESENT INVENTION

--- : MIXED RESIN OF POLYPHENYLENE  
ETHER AND POLYSTYRENE