Abstract:

Disclosed herein is a flameproof copolymer comprising repeating units of (A) about 80-99 % by weight of a (meth)acrylic monomer and (B) about 1-20 % by weight of a vinyl-containing phosphorous monomer. The present invention also provides a thermoplastic resin having good flame retardancy by using the flameproof copolymer.
Description

FLAMEPROOF COPOLYMER AND FLAME RETARDANT THERMOPLASTIC RESIN COMPOSITION USING THEREOF

Technical Field

[1] The present invention relates to a flameproof copolymer and flame retardant thermoplastic resin composition including the same. More particularly, the present invention relates to a flameproof copolymer which comprises a vinyl-containing phosphorous monomer having a specific structure and an acryl monomer and relates to a flame retardant thermoplastic resin composition including the same.

[2] Background Art

[3] In general, acryl monomer resin has good transparency, weatherability, mechanical properties, and excellent thermal stability. Therefore, acryl monomer resins have been widely used in electronic articles, display parts, optical materials, architectural parts, and automobile parts as well as conventional molded articles. In particular, acryl resin has such good scratch resistance that the use thereof has been growing in external parts of electric or electronic goods. However, acryl resins are typically flammable, which restricts their application ranges.

[4] Even though the method of blending an additive-type flame retardant was proposed to improve the flame retardancy of acryl resins, a large amount of flame retardants is needed in order to obtain an aimed level of flame retardancy. The method also had a problem of bad appearance due to the dissolution of flame retardant. Furthermore, it had a problem of reducing acryl-based resin's own properties such as transparency, heat resistance, and mechanical properties.

[5] Therefore, the method of introducing a phosphorous flame retardant to a polymer chain was proposed to solve those problems.

[6] U.S. Patent No. 4,035,571 discloses a flameproof copolymer prepared by copolymerizing unsaturated monomer, bis(hydrocarbyl) vinyl phosphonate, and acrylic acid or methacrylic acid.

[7] However, the method has the problem of using a lot of bis(hydrocarbyl)vinyl phosphonate to obtain enough flame retardancy. This results in bad mechanical properties and also restricts the range of applications.

[8] Accordingly, the present inventors have developed a flameproof copolymer and flame retardant thermoplastic resin composition including the same having good flameproof, transparency, and scratch resistance while maintaining mechanical properties, which are prepared by copolymerizing (meth)acrylic monomer with vinyl-
containing phosphorous monomer having a specific structure with 18~30 % by weight of phosphorus.

[9] Disclosure of Invention

Technical Problem

[10] An object of the present invention is to provide a thermoplastic resin composition having good flame retardancy.

[11] Another object of the present invention is to provide a thermoplastic resin composition having good transparency and scratch resistance, as well as good flame retardancy.

[12] A further object of the present invention is to provide an environmentally friendly thermoplastic resin composition which does not generate toxic gases such as dioxin, furan, or halogenated hydrogen gas at the time of combustion.

[13] A further object of the present invention is to provide a thermoplastic resin composition having a good balance of physical properties.

[14] Other objects and advantages of this invention will be apparent from the ensuing disclosure and appended claims.


[16] One aspect of the invention provides a flameproof copolymer which comprises repeating units of (a) about 80~99 % by weight of a (meth)acrylic monomer and (b) about 1~20 % by weight of a vinyl-containing phosphorous monomer.

[17] In an exemplary embodiment of the invention, the vinyl-containing phosphorous monomer (b) may contain about 18~30 % by weight of phosphorus.

[18] Another aspect of the present invention relates to a method for preparing a flameproof copolymer. The method comprises copolymerizing a (meth)acrylic monomer and a vinyl-containing phosphorous monomer at about 60~90 °C for about 1~6 hours in the presence of a radical initiator.

[19] Furthermore, the present invention provides a flame retardant thermoplastic resin composition containing the foregoing flameproof copolymer. The resin composition may have a haze of about 2 % or less as measured by a Nippon Denshoku Haze meter using a 3 mm thick test sample, a pencil hardness of about 2H measured by JIS K 5401, an Izod impact strength of about 1.3 kgf-D/D or more measured by ASTM D-256 using 1/8" thick test sample, heat resistance (VST) of about 97 °C or more measured by ASTM D-1525 using 1/4" thick test sample, and a flame retardancy of V-2, V-1 or V-O measured by UL 94 using 2.0 mm thick test sample.

[20] The resin composition of the invention may further include an additive selected
from the group consisting of impact modifiers, anti-dripping agents, phenol resins, flame retardants, flame retardant aids, lubricants, antioxidants, plasticizers, thermal stabilizers, light stabilizers, pigments, dyes, inorganic fillers and mixtures thereof.

[21] In an exemplary embodiment of the invention, the amount of the impact modifier may be about 30 parts by weight or less, per 100 parts by weight of the flameproof copolymer. A rubber modified graft copolymer may be used as the impact modifier.

[22] In an exemplary embodiment of the invention, the amount of the anti-dripping agent may be about 2 parts by weight or less, per 100 parts by weight of flameproof copolymer.

[23] In an embodiment, the amount of the phenol resin may be about 1~20 parts by weight, per 100 parts by weight of flameproof copolymer.

[24] In another embodiment, the resin composition may have a haze of about 17 % or less measured by a Nippon Denshoku Haze meter using a 3 mm thick test sample, a pencil hardness of about 2H or more measured by JIS K 5401, an Izod impact strength of about 1.3 kgf-D/D or more measured by ASTM D-256 using a 1/8" thick test sample, heat resistance (VST) of about 95 °C or more measured by ASTM D-1525 using a 1/4" thick test sample, and a flame retardancy of V-2, V-1 or V-O measured by UL 94 using a 2.0 mm thick test sample.

[25] Further, the present invention provides a molded article of the resin composition.

[26] **Best Mode for Carrying Out the Invention**

[27] The flameproof copolymer according to the invention comprises repeating units of (a) (meth)acrylic monomer and (b) vinyl-containing phosphorous monomer.

[28] Examples of the (meth)acrylic monomer (a) may include but are not limited to acrylate, alkyl acrylate, (meth)acrylate, alkyl(meth)acrylate, or (meth)acrylic acid. Those can be used alone or in combination with one another. The preferable (meth)acrylic monomer can be (meth)acrylate, methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, butyl(meth)acrylate, pentyl(meth)acrylate, cyclohexyl(meth)acrylate, n-hexyl(meth)acrylate, glycidyl(meth)acrylate, (meth)acrylic acid or mixtures of thereof.

[29] The vinyl-containing phosphorous monomer (b) can be one or more selected from the compounds represented by chemical formulae 1~4.

[30] [Chemical Formula 1]

[32]
In the above chemical formulae 1~4, $R_1$ is hydrogen or methyl, $R_2$ and $R_3$ are independently methyl or ethyl, and $n$ is 0 or 1.

Examples of the compound represented by chemical formula 1 may be dimethylvinylphosphineoxide, ethylmethylvinylphosphineoxide, diethylvinylphosphineoxide, dimethyl 2-methylvinylphosphineoxide, ethylmethyl 2-methylvinylphosphineoxide, diethyl 2-methylvinylphosphineoxide, dimethylvinylphosphinate, ethylmethylvinylphosphinate, diethylvinylphosphinate, dimethyl 2-methylvinylphosphinate, ethylmethyl 2-methylvinylphosphinate, diethyl 2-methylvinylphosphinate, dimethylvinylphosphonate, ethylmethylvinylphosphonate, diethylvinylphosphonate, dimethyl 2-methylvinylphosphonate, ethylmethyl 2-methylvinylphosphonate, or diethyl 2-methylvinylphosphonate.

Examples of the compound represented by chemical formula 2 may be allyldimethylphosphineoxide, allylmethylethylphosphineoxide, allyldiethylphosphineoxide, 2-methylallyldimethylphosphineoxide.
2-methylallylmethylethylphosphineoxide, 2-methylallyldiethylphosphineoxide, al-
lyldimethylphosphinate, allylmethylethylphosphinate, allyldiethylphosphinate,
2-methylnanyldimethylphosphinate, 2-methylallylallymethylethylphosphinate,
allyldimethylphosphonate, allylmethylethylphosphonate, allyldiethylphosphonate,
2-methylallyldimethylphosphinate, 2-methylallylmethylethylphosphinate, or
2-methylallyldiethylphosphonate.

Examples of the compound represented by chemical formula 3 may be
vinyldimethylphosphinate, vinylethylmethylphosphinate, vinyldiethylphosphinate,
2-methylvinyldimethylphosphinate, 2-methylvinylmethylethylphosphinate, or di-
dimethylvinylphosphate, ethylmethylvinylphosphate, diethylvinylphosphate, dimethyl
2-methylvinyldimethylphosphinate, 2-methylvinylethylmethylphosphonate,
2-methylvinyldiethylphosphonate, 2-methylvinylphosphate.

Examples of the compound represented by chemical formula 4 may be al-
lyldimethylphosphinate, allylethylmethylphosphinate, allyldiethylphosphinate,
2-methylallyldimethylphosphinate, 2-methylallylmethylethylphosphinate,
2-methylallyldiethylphosphinate, allyldimethylphosphonate, allylethyl-
allyldimethylphosphonate, allyldiethylphosphonate, 2-methylallyldimethylphosphonate,
2-methylvinyldimethylphosphonate, 2-methylallyldiethylphosphonate,
allyldimethylphosphate, allylethylmethylphosphate, allyldiethylphosphate,
2-methylallyldimethylphosphate, 2-methylallylmethylphosphonate, or di-
methylallyldiethylphosphonate.

The vinyl-containing phosphorous monomer (b) may preferably contain about
18~30 % by weight of phosphorus in the structure thereof, more preferably about
20~29 % by weight of phosphorus. If the vinyl phosphorous compound containing less
than about 18 % by weight of phosphorus is employed, the copolymer cannot have
sufficient flame retardancy. Furthermore, if the vinyl phosphorous compound
containing more than about 30 % by weight of phosphorus is employed, the com-
patibility can be lowered.

In an embodiment of the present invention, the copolymer may comprise repeating
units of about 80~90 % by weight of a (meth)acrylic monomer and about 5~20 % by
weight of a vinyl-containing phosphorous monomer. When the vinyl-containing
phosphorous monomer is employed within those ranges, high flame retardancy and
good mechanical properties may be obtained. It is more preferable to have about
85~95 % by weight of a (meth)acrylic monomer and about 5~15 % by weight of a
vinyl-containing phosphorous monomer.

An example of a preferred vinyl-containing phosphorous monomer (c) may be dimethylvinylphosphonate (DMVP). The method for preparing the vinyl-containing phosphorous monomer (c) is disclosed in Japanese Patent No. 3836459 the teachings of which are incorporated herein by reference in their entirety.

The flameproof copolymer of the present invention can be prepared by a conventional copolymerization in which the vinyl-containing phosphorous monomer is added to the (meth)acrylic monomer in the presence of a radical initiator. Since the vinyl-containing phosphorous monomer has a polymerizable vinyl group, the vinyl-containing phosphorous monomer and the (meth)acrylic monomer can form a main chain together. An unsaturated group containing monomer, for example, an aromatic vinyl monomer can be optionally added while copolymerizing. The amount of the (meth)acrylic monomer and the vinyl-containing phosphorous monomer may be controlled by adding until the repeating unit of the final copolymer could reach the level of the ratio stated above.

In an embodiment of the present invention, a (meth)acrylic monomer and a vinyl-containing phosphorous monomer may be added to a reactor, followed by copolymerizing at about 60–90 °C for about 1 to 6 hours in the presence of an initiator.

The suitable initiators may be, but are not limited to, radical initiators such as benzoyl peroxide (BPO), dicumylperoxide (DCP), di-tert-butylperoxide (DTBP), azobisisobutyronitrile (AIBN), and the like.

The flameproof copolymer of the present invention can be used in place of a conventional acrylic resin. For example, the flameproof copolymer may be used alone, or used as a thermoplastic resin composition by blending with other resins or additives to improve the impact strength and flame retardancy.

Impact modifier

The flame retardant thermoplastic resin composition of the present invention may further comprise an impact modifier according to the needs. The impact modifier may be a polymer prepared by grafting the rubber polymer with a vinyl monomer. The impact modifier may be prepared by graft copolymerizing an aromatic vinyl monomer and optionally a copolymerizable monomer onto a rubber polymer.

The rubber may be at least one rubber polymer selected from the group consisting of diene-based rubber such as polybutadiene rubber, poly(styrene-butadiene) rubber, and poly(acrylonitrile-butadiene) rubber, saturated rubber in which hydrogen is added to a diene rubber, isoprene rubber, acrylic rubber, silicon rubber, ethylene/propylene rubber, and ethylene-propylene-diene terpolymer (EPDM). Among these rubbers, the
diene-based rubber is preferable, and the butadiene-based rubber is more preferable. The preferable amount of rubber is about 5 to about 65 % by weight, per 100 % by weight of a graft copolymer resin. The rubber polymer may have preferably an average particle size of about 0.1~4 D considering the impact strength and the appearance of a molded article. The impact modifier may be used in the range of about 30 parts by weight or less on the basis of 100 parts by weight of the flameproof copolymer, preferably about 0.1 to 20 parts by weight, and more preferably about 0.5 to 15 parts by weight. If the amount of the impact modifier is more than 30 parts by weight, the flame retardancy can be lowered.

Anti-dripping agent

The flame retardant thermoplastic resin composition of the present invention can further include an anti-dripping agent according to the needs. The anti-dripping agent may be an additive which can exist in the form of fiber in the resin phase, after a mixing process with resin. Examples thereof may be fluoro-based resin, for example, polytetrafluoroethylene, a copolymer of tetrafluoroethylene and hexafluoropropylene, a fluorinated carbon resin of tetrafluoroethylene and perfluoroalkylvinylether, and polyvinylidene fluoride.

The anti-dripping agent can be preferably used in the range of about 2 parts by weight or less per 100 parts by weight of the flameproof copolymer. When the anti-dripping agent is used over 2 parts by weight, the impact resistance may be deteriorated. Among the fluoro-based resins, polytetrafluoroethylene is preferred.

Phenol resin

The resin composition of the present invention may further include a phenol resin as a char forming agent. Since the phenol resin can form a char at low temperature (about 300~450 °C), it may play an effective role in forming char on the surface in early combustion.

Phenol resins are generally classified into resol-type phenolic resins and novolak-type phenolic resins. In the present invention, the novolak-type phenolic resins are particularly more preferable than the resol-type phenolic resins. The novolak-type phenolic resins may include phenol formaldehyde novolak resin, tertiarybutylphenol formaldehyde novolak resin, para octylphenol formaldehyde novolak resin, para cyanophenol formaldehyde novolak resin, phenolepoxy novolak resin, and mixtures thereof. It is preferable that the novolak-type phenolic resin has a weight average molecular weight (Mw) of about 300 to about 10,000.
The phenol resin may comprise about 1 to about 20 parts by weight per 100 parts by weight of the flameproof copolymer, preferably about 1 to about 10 parts by weight. If the amount of the phenol resin is more than about 20 parts by weight, the mechanical properties may be degraded, and weatherability may be lowered.

The resin composition of the invention may further include an additive selected from the group consisting of flame retardants, flame retardant aids, lubricants, antioxidants, plasticizers, thermal stabilizers, light stabilizers, inorganic fillers, pigments, dyes. These additives can be used alone or in combination with one another.

The flame retardant can be a phosphorous flame retardant or a halogen flame retardant, preferably phosphorous flame retardant. Examples of the phosphorous flame retardant may include red phosphorus, phosphate, phosphonate, phosphinate, phosphine oxide, phosphazene, a metal salt thereof, and the like. Among those, aromatic phosphoric acid ester (phosphate) compound is most preferred.

The flame retardant may be used preferably in the range of about 30 parts by weight or less per 100 parts by weight of the flameproof copolymer, more preferably about 0.1 to 15 parts, most preferably about 0.3 to 10 parts by weight. If the amount of the flame retardant is more than 30 parts by weight, mechanical properties such as flame retardancy and impact strength may be degraded.

The resin composition according to the present invention can be prepared by a conventional process. For example, all the components and additives can be mixed together and extruded through an extruder and can be prepared in the form of pellets.

Further, the resin composition according to the present invention may be used in various molded products. In particular, the resin composition is suitable for the production of electric and electronic goods such as housings of TV, computers, audio sets, air conditioners, office automation devices, and the like.

The invention may be better understood by reference to the following examples which are intended for the purpose of illustration and are not to be construed as in any way limiting the scope of the present invention, which is defined in the claims appended hereto.

Mode for the Invention

Examples

Example 1

90 parts by weight of methylmethacrylate, 10 parts by weight of
dimethylvinylphosphonate containing 22.76 % by weight of phosphorus, and 0.3 parts
by weight of benzoyl peroxide were added into a reactor, and stirred to react at 80 °C for 3 hours. The resulting polymer was dried in a vacuum oven to obtain a flame retardant PMMA copolymer (VP-PMMA). Then, the VP-PMMA copolymer was extruded through a twin screw extruder in pellets at 200~260 °C. The pellets were molded into test specimens using a 8 oz injection molding machine at 250 °C with a barrel temperature of 60 °C.

Example 2

Example 2 was conducted in the same manner as in Example 1 except that 5 parts by weight of EXL-2602 (methyl methacrylate-butadiene-acrylate copolymer) manufactured by MRC Co. was further added as an impact modifier.

Example 3

Example 3 was conducted in the same manner as in Example 2 except that 0.5 parts by weight of polytetrafluoroethylene (Teflon 30J manufactured by Mitsui-Dupont Company) was further added as an anti-dripping agent.

Example 4

Example 4 was conducted in the same manner as in Example 1 except that 0.5 parts by weight of polytetrafluoroethylene (Teflon 30J manufactured by Mitsui-Dupont Company) was further added as an anti-dripping agent.

Comparative Example 1

Comparative Example 1 was conducted in the same manner as in Example 1 except that 75 parts by weight of a conventional PMMA copolymer (L-84 manufactured by LG Chem Co. of Korea) not containing dimethylvinylphosphonate was used instead of the flame retardant PMMA copolymer of the present invention, and that 25 parts by weight of resorcinol bis(2,6 dimethylphenylphosphate) (PX-200 manufactured by Daihachi Chemical Co. of Japan) was added as a flame retardant.

Comparative Example 2

Comparative Example 2 was conducted in the same manner as in Comparative Example 1 except that 5 parts by weight of EXL-2602 (methyl methacrylate-
butadiene-acrylate copolymer) manufactured by MRC Co. was further added as an impact modifier.

**Comparative Example 3**

Comparative Example 3 was conducted in the same manner as in Comparative Example 2 except that 0.5 parts by weight of polytetrafluoroethylene (Teflon 30J manufactured by Mitsui-Dupont Company) was further added as an anti-dripping agent.

**Comparative Example 4**

Comparative Example 4 was conducted in the same manner as in Comparative Example 1 except that 0.5 parts by weight of polytetrafluoroethylene (Teflon 30J by Mitsui-Dupont) was further added as an anti-dripping agent.

The physical properties of the test specimens produced by the Examples and Comparative Examples were measured as follows and the test results were shown in Table 1 below.

(1) Haze (%): The Haze (%) was measured by Nippon Denshoku Haze meter using a 3 mm thick test sample.

(2) Pencil Hardness: The pencil hardness was measured for the specimens of 10x10 d. after exposure at 23 °C and 50 % of relative humidity for 48 hours in accordance with JIS K 5401. The scratch resistance was measured by 3B, 2B, B, HB, F, H, 2H, 3H, etc. The higher the H value, the better the scratch resistance is. The higher the B value, the lower the scratch resistance is.

(3) Izod Impact Strength: The notch Izod impact strength was measured in accordance with ASTM D-256 (1/4 inch, kgf-D/D).

(4) Heat Resistance (VST): The Vicat Softening Temperature was measured in accordance with ASTM D-1525 (1/4" inch, kgf-D/D) under 5 kgf load (°C).

(5) Flame Retardancy: The flame retardancy was measured in accordance with UL 94 using a 2.0 mm thick test sample.

Table 1

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<thead>
<tr>
<th>Examples</th>
<th>comparative examples</th>
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<td>1 2 3 4</td>
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As shown in Table 1, Example 1 shows good transparency, pencil hardness, and heat resistance due to low haze. Example 2 shows low but enough transparency as it contains an impact modifier, and shows a good balance of physical properties such as impact strength and flame resistance. Example 3~4 employing PTFE as an anti-dripping agent show little change of physical properties, and show upgrading of flameproof to V1 and V0 as compared to Examples 1~2. On the other hand, Comparative Examples 1~4 using conventional PMMA show low flame retardancy and low flame resistance even though they contain the same amount of phosphorus as Examples 1~4 have. They also show that flame resistance is dramatically lowered.

In the above, the present invention was described based on the specific preferred embodiments, but it should be apparent to those ordinarily skilled in the art that various changes and modifications can be added without departing from the spirit and scope of the present invention which will be defined in the appended claims.
Claims

[1] A flameproof copolymer comprising repeating units of:
(A) 80 to 99 % by weight of a (meth)acrylic monomer; and
(B) 1 to 20 % by weight of a vinyl-containing phosphorous monomer.

[2] The flameproof copolymer of claim 1, wherein said vinyl-containing phosphorous monomer (B) is at least one selected from the compounds represented by chemical formulae 1~4:

[Chemical Formula 1]

[Chemical Formula 2]

[Chemical Formula 3]

[Chemical Formula 4]

wherein R is hydrogen or methyl, R and R are independently methyl or ethyl, and n is 0 or 1.

[3] The flameproof copolymer of claim 1, wherein said vinyl-containing phosphorous monomer (B) contains 18~30 % by weight of phosphorus.

[4] The flameproof copolymer of claim 1, wherein said (meth)acrylic monomer (A) is selected from the group consisting of (meth)acrylate, methyl(meth)acrylate, ethyl(meth)acrylate, propyl(meth)acrylate, butyl(meth)acrylate, pentyl(meth)acrylate, cyclohexyl(meth)acrylate, n-hexyl(meth)acrylate, glycidyl(meth)acrylate, (meth)acrylic acid and mixtures thereof.

[5] A flame retardant thermoplastic resin composition comprising the flameproof
copolymer as defined in any one of claims 1-4.

[6] The flame retardant thermoplastic resin composition of claim 5, wherein said
resin composition has a haze of 2% or less as measured by a Nippon Denshoku
Haze meter using a 3 mm thick test sample, a pencil hardness of 2H measured by
JIS K 5401, an Izod impact strength of 1.3 kgf-D/D or more measured by ASTM
D-256 using 1/8" thick test sample, heat resistance (VST) of 97 °C or more
measured by ASTM D-1525 using 1/4" thick test sample, and a flame retardancy
of V-2, V-I or V-O measured by UL 94 using 2.0 mm thick test sample.

[7] A molded article produced from the flame retardant thermoplastic resin
composition as defined in claim 5.

[8] The flame retardant thermoplastic resin composition of claim 5, further
comprising at least one additive selected from the group consisting of impact
modifier, anti-dripping agent, phenol resin, flame retardant, flame retardant aid,
lubricant, antioxidant, plasticizer, thermal stabilizer, light stabilizer, pigment,
dye, inorganic filler and mixtures thereof.

[9] The flame retardant thermoplastic resin composition of claim 8, wherein said
impact modifier is used in the range of 30 parts by weight or less, per 100 parts
by weight of the flameproof copolymer.

[10] The flame retardant thermoplastic resin composition of claim 8, wherein said
anti-dripping agent is used in the range of 2 parts by weight or less, per 100 parts
by weight of the flameproof copolymer.

[11] The flame retardant thermoplastic resin composition of claim 8, wherein said
phenol resin is used in the range of 1-20 parts by weight or less, per 100 parts by
weight of the flameproof copolymer.

[12] The flame retardant thermoplastic resin composition of claim 8, wherein said
resin composition has a haze of 17% or less measured by a Nippon Denshoku
Haze meter using a 3 mm thick test sample, a pencil hardness of 2H or more
measured by JIS K 5401, an Izod impact strength of 1.3 kgf-D/D or more measured
by ASTM D-256 using a 1/8" thick test sample, heat resistance (VST) of 95 °C or
more measured by ASTM D-1525 using a 1/4" thick test sample, and a flame retardancy
of V-2, V-I or V-O measured by UL 94 using a 2.0 mm thick test sample.

[13] A molded article produced from the flame retardant thermoplastic resin
composition as defined in claim 8.

[14] A method for preparing a flameproof copolymer comprising: copolymerizing a
(meth)acrylic monomer and a vinyl-containing phosphorous monomer at 60-90
°C for 1-6 hours in the presence of a radical initiator.
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

C08F 230/02(2006.01)
i

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 8 C08F

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 practicable, search terms used)
eKIPASS, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
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<td>X Y</td>
<td>JP63-095249 A (MITSUBISHI RAYON CO LTD) 26 Apr 1988 Claims 1-5</td>
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<td>Y</td>
<td>US5292817 A (Arco Chemical Technology, L P ) 08 Mar 1994 Abstract, Claims 1-14</td>
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<td>US3965216 A (Stauffer Chemical Company) 22 Jun 1976 Abstract, Claims 1-5</td>
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<td>JP56-161414 A (KAO CORP) 11 Dec 1981 Claims 1-3</td>
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* Special categories of cited documents
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of citation or other special reason (as specified)
"O" document referring to an oral disclosure use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

Further documents are listed in the continuation of Box C

See patent family annex

Date of the actual completion of the international search
19 MARCH 2008 (19.03.2008)

Date of mailing of the international search report
19 MARCH 2008 (19.03.2008)

Name and mailing address of the ISA/KR
Korean Intellectual Property Office
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Facsimile No 82-42-472-7140

Authorized officer
KANG, HYUNG SEOK
Telephone No 82-42-481-5597

Form PCT/ISA/210 (second sheet) (April 2007)
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