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(54) Title: MACROMONOMERS HAVING REACTIVE SIDE GROUPS (57) Abstract Rigid-rod macromonomers, and methods for preparing such macromonomers, having a polyaromatic backbone, solubilizing side groups, and reactive side groups are provided. The macromonomers are chemically incorporated into polymer systems to provide stronger, stiffened polymers.		

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MACROMONOMERS HAVING REACTIVE SIDE GROUPS

Field of the Invention

This invention relates to soluble macromonomers having rigid-rod backbones, pendant, flexible, solubilizing organic groups attached to the backbone, and pendant reactive groups attached to the backbone of the macromonomer chains. They can be chemically incorporated into other polymer and monomer systems to yield strengthened, stiffened polymer compositions.

20

Background of the Invention

It is well known that the stiffness and strength of a polymer are related to the flexibility of the polymer chain on the molecular level. Thus, if the chemical structure of the main chain restricts chain coiling and flexing, the resulting polymer will be stiff and strong. An example of a stiff polymer is poly-1,4-phenylene-1,4-terephthalamide (PPTA). While PPTA can coil in solution, the amide linkages and para-phenylene groups favor an extended chain conformation. Fibers can be prepared in which the chains are essentially all extended into rod-like conformations, and these fibers are extraordinarily strong and stiff. Unfortunately, PPTA is difficult to process (except for fiber spinning) and cannot be molded or extruded. In general, the more rigid the polymer main chain the more difficult it is to prepare and process.

35

1 Some applications require strong, stiff materials
that can be easily processed by molding or extrusion. A
widely used approach to obtain such stiff materials is to
add fillers such as carbon or silica, or to incorporate
5 fibers, such as glass and carbon fibers, into a relatively
flexible polymer, thereby forming a stiff, strong
composite material. The most widely utilized, high-
performance fiber-polymer composites are composed of
oriented carbon (graphite) fibers embedded in a suitable
10 polymer matrix.

 The improvements in strength and stiffness of
composites are related to the aspect ratio of the filler
or fiber, i.e., the length to diameter ratio of the
smallest diameter cylinder that will enclose the filler
15 or fiber. To contribute reasonable strength and stiffness
to the composite, the fibers must have an aspect ratio of
at least about 25, and preferably at least 100.
Continuous fibers have the highest aspect ratio and yield
the best mechanical properties but are costly to process.
20 Low aspect ratio materials, such as chopped fibers and
fillers, give limited improvement in mechanical
properties, but are easy and inexpensive to process. The
success of composites is demonstrated by their wide use
as structural materials.

25 There are several drawbacks associated with composite
materials. Composites are often more costly than the un-
reinforced polymer. This is because of the expense of
the fiber component and the additional labor needed to
prepare the composite. Composites are difficult or
30 impossible to repair and in general cannot be recycled.
Many composites also have undesirable failure
characteristics, failing unpredictably and
catastrophically.

 Molecular composites (composed of polymeric materials
35 only) offer the prospect of high performance, lower cost
and easier processability than conventional fiber-polymer
composites. In addition, molecular composites generally

1 can be recycled and repaired. Because molecular
composites contain no fibers, they can be fabricated much
more easily than fiber-polymer compositions, which contain
macroscopic fibers.

5 Molecular composites are materials composed of a
rigid-rod polymer embedded in a flexible polymer matrix.
The rigid-rod polymer in a molecular composite can be
thought of as the microscopic equivalent of the fiber in
a fiber-polymer composite. The flexible polymer component
10 of a molecular composite serves to disperse the rigid-rod
polymer, preventing bundling of the rigid-rod molecules.
As in conventional fiber/resin composites, the flexible
polymer in a molecular composite helps to distribute
stress along the rigid-rod molecules via elastic
15 deformation of the flexible polymer. Thus, the second,
or matrix-resin polymer must be sufficiently flexible to
effectively surround the rigid-rod molecules while still
being able to stretch upon stress. The flexible and
rigid-rod polymers can also interact strongly via Van der
20 Waals, hydrogen bonding, or ionic interactions. The
advantages of molecular composites over fiber-based
composites are realized by incorporating rigid-rod
segments into polymer systems. The advantages of
molecular composites have been demonstrated by, e.g., W.F.
25 Hwang, D.R. Wiff, C.L. Benner and T.E. Helminiak, Journal
of Macromolecular Science. - Phys., B22, 231-257 (1983).

 Molecular composites are simple mixtures or blends
of a rigid-rod polymer with a flexible polymer. As is
known in the art, most polymers do not mix with other
30 polymers, and attempts at blends lead to macroscopic phase
separation. This is also true of rigid-rod
polymer/flexible polymer blends. Metastable blends may
be prepared by rapid coagulation from solution. However,
metastable blends will phase separate on heating, ruling
35 out further thermal processing, such as molding or melt
spinning and use at high temperatures. The problem of
macroscopic phase separation is reported in H.H. Chuah,

1 T. Kyu, and T.E. Helminiak, Polymer, 28, 2130-2133 (1987).
Macroscopic phase separation is a major limitation of
molecular composites.

5 Rigid-rod polymers produced in the past are, in
general, highly insoluble (except in the special case of
polymers with basic groups, which may be dissolved in
strong acids or in organic solvents with the aid of Lewis
acids) and infusible. Preparation and processing of such
10 polymers is, accordingly, difficult. A notable exception
is found in U.S. patent application Serial No. 07/397,732,
filed August 23, 1989 (assigned to the assignee of the
present invention), which is incorporated herein by this
reference. The rigid-rod polymers described in the above-
referenced application have a rigid-rod backbone
15 comprising a chain length of at least 25 organic monomer
units joined together by covalent bonds wherein at least
about 95% of the bonds are substantially parallel; and
solubilizing organic groups attached to at least 1% of the
monomer units. The polymers are prepared in a solvent
20 system that is a solvent for both the monomer starting
materials and the rigid-rod polymer product. The
preferred monomer units include: paraphenyl,
parabiphenyl, paraterphenyl, 2,6-quinoline,
2,6-quinazoline, paraphenylene-2-benzobisthiazole,
25 paraphenylene-2-benzobisoxazole, paraphenylene
-2-benzobisimidazole, paraphenylene-1-pyromellitimide,
2,6-naphthylene, 1,4-naphthylene, 1,5-naphthylene,
1,4-anthracenyl, 1,10-anthracenyl, 1,5-anthracenyl,
2,6-anthracenyl, 9,10-anthracenyl, and 2,5-pyridinyl.

30 The rigid-rod polymers described above can be used
as self-reinforced engineering plastics and exhibit
physical properties and cost-effectiveness superior to
that exhibited by many conventional fiber-containing
composites. It would be quite useful if rigid-rod
35 polymers could be incorporated into conventional flexible
polymers, especially large volume commodity polymers. The
value of a flexible polymer would be increased

1 significantly if its mechanical properties could be
enhanced by addition of rigid-rod polymers. Such
molecular composites could displace more expensive
engineering resins and specialty polymers and conventional
5 composites as well. To date, practical molecular
composites have not been demonstrated. This is chiefly
due to deficiencies in currently available rigid-rod
polymers, namely, limited solubility and fusibility and
unfavorable chemical and physical interactions between the
10 rigid-rod and the flexible polymer component.

There is a need in the art for a rigid-rod polymer
that can be chemically incorporated into flexible polymers
and polymer systems, during or subsequent to
polymerization, to thereby add strength and/or stiffness
15 to the resulting polymers. Chemical rather than physical
incorporation is desirable to inhibit phase separation
during the processing and use of the polymer and to
increase the resulting polymer's solvent resistance. The
mechanical behavior of polymer systems which contain
20 chemically incorporated rigid-rod moieties can be
different and superior to physical blends of, for example,
rigid-rod polymers with flexible polymers.

Summary of the Invention

25 It has now been found that, for any given polymer,
improvements in stiffness and strength can be obtained by
preparing a copolymer, thermoset resin, or the like, which
incorporates rigid segments and the more flexible segments
of the original polymer. These rigid segments act in a
30 manner conceptually similar to the way stiff fibers act
to reinforce composites; however, in the present invention
no macroscopic fibers are present.

In the present invention, the problem of macroscopic
phase separation, found in molecular composites, is
35 avoided by the use of rigid-rod macromonomers having
reactive side groups. In one embodiment of the present
invention, the rigid-rod macromonomers are made to react

1 with flexible polymers, via reactive side groups, to form
covalent bonds between the rigid-rod macromonomer and the
flexible polymer, thereby preventing macroscopic phase
separation.

5 In a second embodiment, macroscopic phase separation
is prevented by forming the flexible polymer in the
presence of the macromonomer. The reactive side groups
of the macromonomer react with monomers during
polymerization of the flexible polymer, forming covalent
10 bonds between the macromonomer and flexible polymer.

In a third embodiment, the rigid-rod macromonomer is
modified, by way of chemical transformation of its
reactive side groups, such that the side groups are made
compatible with the flexible polymers. Compatibilizers
15 include groups which will interact with the flexible
polymer ionically, by hydrogen bonding, or by van der
Waals interactions. Compatibilizers may be polymeric or
oligomeric. For example, a rigid-rod macromonomer may be
made to react, via its reactive side groups, with
20 caprolactam to form short polycaprolactam chains at
various locations along the macromonomer chain, the
resulting polycaprolactam-modified macromonomer being
compatible with polycaprolactam.

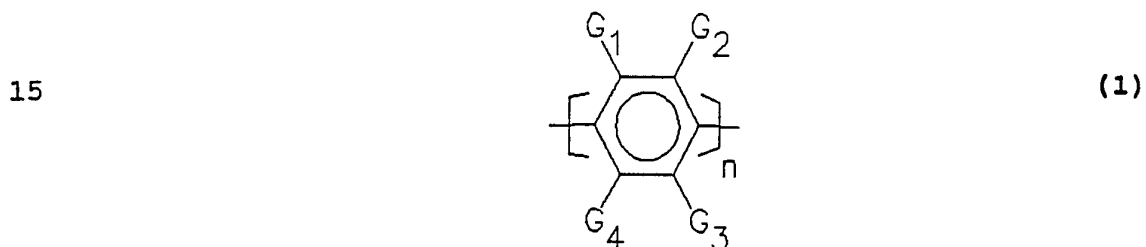
It should be understood that while macroscopic phase
25 separation is prevented, there may be varying degrees of
microscopic phase separation. Microscopic phase
separation results in the formation of phases that have
sizes on the order of the dimensions of the polymer chain.
Microphase separation may be conducive to significant
30 improvements in mechanical or other properties desired
from incorporation of rigid-rod macromonomers.

In a fourth embodiment, the rigid-rod macromonomers
are used alone as thermosetting resins. In this case, the
side groups provide some degree of processability and will
35 react under the appropriate conditions (e.g. heat,
irradiation, exposure to air, etc.) to form crosslinks and
effect curing.

1 In a fifth embodiment, the rigid-rod macromonomers
are used to modify ceramics and inorganic glasses, using
sol-gel or other methods known in the art. Here, the
reactive side groups undergo special interactions with the
5 inorganic matrix, either polar, ionic or covalent.

Other methods of incorporating the rigid-rod
macromonomers of the present invention into materials are
contemplated and depend on the chemistry and properties
of the material to be modified.

10 In one embodiment of the invention, the macromonomers
have the structure (1):



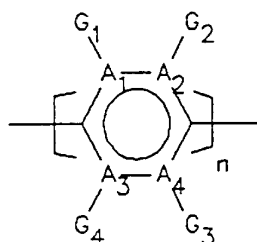
20 where each G_1 , G_2 , G_3 , and G_4 , on each monomer unit,
independently, is either hydrogen, a solubilizing side
group, or a functional ("reactive") side group, and the
number average degree of polymerization, DP_n , is greater
25 than about 6. If DP_n is less than about 7 or 8, the
rigidity and stiffness of polymers incorporating such
macromonomers are only slightly increased. Preferably,
 DP_n is between 10 and 500. In some applications,
however, macromonomers prepared in accordance with the
30 present invention having a DP_n as low as 4 may be useful,
for example, as a means of decreasing the thermal
expansion coefficient of a flexible polymer, such as a
polyimide or a polyamide.

35 At least one monomer unit in the macromonomer has at
least one reactive side group or reactive solubilizing
side group. A description of such groups is provided
below.

1 The structures presented here show only a single
monomer unit and do not imply regular head-to-tail
arrangement of monomer units along the chain. Monomer
units may have random orientation or may be alternating
5 head-to-head, tail-to-tail, or regular head-to-tail, or
have other arrangements, depending on the conditions of
the polymerization and reactivity of monomers.

 The macromonomers of the present invention may also
contain heteroatoms in the main chain. Heteroaromatic
10 rigid-rod macromonomers have structure (2), where A_1 , A_2 ,
 A_3 , and A_4 on each monomer unit, independently, may be
carbon or nitrogen, and each G is as defined above, except
that where an A is nitrogen, the corresponding G is nil.

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(2)

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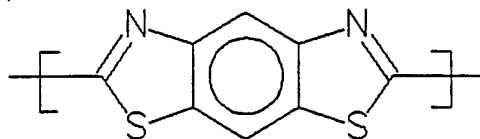
 As with structure (1), the macromonomers of structure
(2) have at least one monomer unit that has at least one
25 reactive side group or reactive solubilizing side group.

 Other rigid-rod monomer units can also be
incorporated into the macromonomers prepared in accordance
with the present invention. Thus a rigid-rod macromonomer
having monomer units of the type shown in structures (1)
30 and/or (2) and benzobisthiazole monomer units

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15 can be used in the same way as (1) and (2). Likewise, rigid-rod pyromellitimide, benzobisoxazole, benzobisimidazole and other rigid-rod monomer units may be substituted for some of the phenylene units without loss of function. The benzobisimidazole, thiazole and
20 oxazole units may have either a cis or trans configuration.

The rigid-rod macromonomers of the present invention may be further polymerized or cured by virtue of their reactive side groups. Depending on the nature of the side
25 groups and cure conditions, branched, network, or other structures result.

The macromonomers of the present invention may be used to form thermosets, either alone or in combination with other thermosetting polymers. The macromonomers may
30 also be used with thermoplastics, e.g., by forming a copolymer.

35

1 Brief Description of the Drawings

 Figure 1 is a schematic illustration of the formation
of a crosslinked polymer prepared by reacting
macromonomers of the present invention with one species
5 of complementary monomers;

 Figure 2 is a schematic illustration of the formation
of a crosslinked polymer prepared by polymerizing
macromonomers of the present invention with two different
species of complementary monomers;

10 Figure 3 is a schematic illustration of the formation
of a graft polymer formed with macromonomers of the
present invention;

 Figure 4 is a schematic illustration of the formation
of a semi-interpenetrating network of an uncrosslinked
flexible polymer in a network of a crosslinked
15 monomer/macromonomer system;

 Figure 5 is a schematic illustration of the formation
of a graft copolymer formed with macromonomers of the
present invention wherein the reactive side groups are
polymerization initiators; and
20

 Figure 6 is a schematic illustration of the formation
of a crosslinked polymeric material made with
macromonomers of the present invention wherein the
reactive side groups can participate in addition type
25 polymerization.

30

35

1 Detailed Description of the Invention

 As discussed above, the strength and stiffness of a polymer are related to the flexibility of the polymer chain on a molecular level. It has now been found that
5 for any given polymer, improvements in stiffness and strength can be obtained by preparing a copolymer having rigid segments as well as the more flexible segments of the original polymer. These rigid segments act in a manner conceptually similar to the way stiff fibers act
10 to reinforce composites, however, in the present invention no macroscopic fibers are present. The rigid segments are provided by incorporating rigid-rod macromonomers having structures (1) and/or (2) during or subsequent to polymerization of the flexible polymer. Several
15 approaches are provided by the present invention.

 Macromonomers having structure (1) are solubilized polyparaphenylenes having reactive functional side groups. Macromonomers having structure (2) are aza derivatives of polyparaphenylenes having reactive side groups. In each
20 case, G_1 through G_4 are solubilizing side groups, functional side groups, or hydrogen, and the number average degree of polymerization, DP_n , is greater than about 6, preferably between 10 and 500.

 The terms "reactive side group," "functional side
25 group," and the like are defined to mean any chemical moiety attached to the backbone of a rigid-rod macromonomer molecule, which chemical moiety can be used in a subsequent reaction to effect one or more of the following reactions:

- 30 a) Reaction with a flexible polymer resulting in formation of one or more covalent bonds between the macromonomer and the flexible polymer;
- b) Reaction with monomers, either before or during
35 a reaction in which such monomers are polymerized to give a flexible polymer, resulting in formation of

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1 one or more covalent bonds between the macromonomer
and the resulting flexible polymer;

5 c) Reaction with an oligomer or other small
molecular species, resulting in increased
compatibility of the rigid-rod macromonomer with
flexible polymers in blends, mixtures, composites,
copolymers, composites, alloys and the like; and

10 d) Polar, ionic, or covalent interaction with an
inorganic matrix, resulting in a modified ceramic or
an inorganic glass or glass-like material.

15 Reactive groups may be transformed by further
chemical reaction, including without limitation,
oxidation, reduction, deprotonation, halogenation, Schiff
base formation, hydrolysis, electrophilic or nucleophilic
substitution, and the like, to yield new reactive groups.

20 One skilled in the art will recognize that it
sometimes will be desirable to incorporate such reactive
side groups in a protected form in order to ensure that
the reactive group does not poison or otherwise
participate in or interfere with the macromonomer-forming
reaction, e.g., an amine can be incorporated as an amide,
25 a carboxylic acid can be incorporated as an ester, and an
alcohol can be incorporated as an ester or as an ether.
Once formation of the macromonomer has been completed the
protected reactive side group can then be deprotected,
e.g., an amide or an ester can be hydrolyzed to produce
30 an amine and an alcohol, respectively.

35 Non-limiting examples of reactive side groups include
acetals, acetals from ethylvinylether, acetylenes,
acetyls, acid anhydrides, acids, acrylamides, acrylates,
alcohols, aldehydes, alkanols, alkyl aldehydes, alkyl
ketones, amides, amines, alkyl halides, anilines, aryl
aldehydes, aryl ketones, azides, benzocyclobutenes,
biphenylenes, carbonates, carboxylates, carboxylic acids

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1 and their salts, carboxylic acid halides, carboxylic
anhydrides, cyanates, cyanides, epoxides, esters, ethers,
formyls, fulvenes, halides, heteroaryls, hydrazines,
5 hydroxylamines, imides, imines, isocyanates, ketals,
ketoalkyls, ketoaryls, ketones, maleimides, nadimides,
nitriles, olefins, phenols, phosphates, phosphonates,
quaternary amines, silanes, silicates, silicones, silyl
ethers, styrenes, sulfonamides, sulfones, sulfonic acids
and their salts, sulfonyl halides, sulfoxides,
10 tetrahydropyranyl ethers, thioethers, urethanes, vinyl
ethers, vinyls and the like. In some cases, the
functional side groups are capable of reacting with each
other. Reactive side groups may be oligomeric or
polymeric. Reactive side groups may also be bridging
15 groups, such as $-\text{CH}_2\text{CH}=\text{CHCH}_2-$.

One skilled in the art will recognize that reactive
groups can be prepared from "non-reactive" groups and
"less reactive" groups. For example, some applications
make it desirable to incorporate a rigid-rod polymer
20 having tolyl end groups into a flexible polyester. The
tolyl group is unreactive toward polyesters or polyester
monomers, however, the tolyl group can be oxidized to a
reactive carboxyphenyl group which then can react with
polyesters by trans-esterification or with polyester
25 monomers to form polyesters containing the rigid-rod
macromonomer. Similarly, a relatively non-reactive acetyl
group can be modified by formation of a Schiff's base with
4-aminophenol, to give a macromonomer having phenolic end
groups, useful for reinforcing thermoset resins such as
30 epoxies and phenolics. Other examples will be apparent
to those skilled in the art.

The term "solubilizing side group" as used herein
means a chemical moiety which, when attached to the
backbone of the macromonomer, improves the solubility of
35 the macromonomer in an appropriate solvent system. For
the purposes of the present invention, the term "soluble"
will mean that a solution can be prepared containing

1 greater than 0.5% by weight of the macromonomer or greater
than about 0.5% of the monomer(s) being used to form the
macromonomer.

5 One skilled in the art will appreciate that various
factors must be considered in choosing a solubilizing
group for a particular polymer and solvent, and that, all
else being the same, a larger or higher molecular weight
solubilizing group will induce a higher degree of
10 solubility. Conversely, for smaller solubilizing groups,
matching the properties of the solvent and solubilizing
groups is more critical, and it may be necessary to have,
in addition, other favorable interactions inherent in the
structure of the polymer to aid in solubilization.

15 For the macromonomers of the present invention any
given non-hydrogen side group G can act as a solubilizing
group, a reactive group, or both a solubilizing and
reactive group; the latter being referred to as a reactive
solubilizing group.

20 The number average degree of polymerization, DP_n , is
defined by:

$$DP_n = (\text{number of monomer molecules present initially}) / (\text{number of polymer or oligomer chains in the system}).$$

25 The number average molecular weight, M_n is defined
by:

$$M_n = M_0 \times DP_n$$

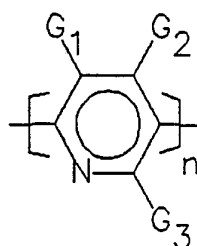
where M_0 is the weight of one monomer unit in the chain.

30 The number average degree of polymerization DP_n is
indicated in structural formulae, as in structure (1), by
"n".

35 Compounds having structure (1) or (2) are solubilized
rigid-rod macromonomers having reactive side groups. Such
macromonomers are rigid or stiff on both the microscopic
and macroscopic level. These macromonomers can be
incorporated into other polymers via the side groups G

1 which are reactive side groups and will impart stiffness
and strength to the resultant polymers. The distinction
between oligomers and polymers is that the properties of
an oligomer change measurably on changing the degree of
5 polymerization by one, while for a polymer adding an
additional monomer unit has little effect on properties.
Since the range of DP_n (>6) considered here covers both
oligomers and polymers, and since this technical
distinction is not of great importance to the applications
10 of these compounds, we will use the term macromonomer to
imply the entire range from oligomers to polymers.

In macromonomers having structure (2), if only one
of the A's is nitrogen, for example if A_4 is N,
substituted polypyridines of structure (3) result:



(3)

25 If only A_1 and A_2 are N, the monomer unit is a
pyridazine; if only A_1 and A_3 are N, the monomer unit is
a pyrazine, if only A_1 and A_4 are N, the monomer unit is
a pyrimidine. If three A's are N, the monomer unit is a
triazine. Other heterocyclic monomer units are included
if some of the G's are bridging, for example, if G_1 and G_2
30 are $-CHCHCHCH-$, and A_3 is N, the monomer unit is an
isoquinoline.

Macromonomers having the structure (2) include
compounds of the structure (1) as a subset.

35 It is possible to have rigid-rod macromonomers in
accordance with the present invention comprising several
types of monomer units, each with a different set of A's
and G's, i.e., each A_1 , A_2 , A_3 and A_4 on each monomer unit,

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1 independently is C or N, and each G_1 , G_2 , G_3 , and G_4 on
each monomer unit, independently is H, a solubilizing side
group, or a reactive side group. In other words, adjacent
monomer units need not be identical. Macromonomers
5 comprised of different monomers are copolymer-type
macromonomers.

As stated above, the number and type of side groups
necessary to impart solubility will depend on n and the
nature and number of reactive side groups. If n is small,
10 only a few side chains will be needed for solubility.
That is, only some of the monomer units in each chain may
be substituted; the rest are either unsubstituted, i.e.,
the G 's are all H, or are non-solubilizing reactive side
groups. Where n is very small and the reactive side
15 groups aid solubility, few "solubilizing" side groups are
required. Where n is large, solubility may be maintained
by using more non-H G 's per chain or by using G 's with
higher molecular weight. In many cases, the macromonomer
will have exactly one non-hydrogen G per monomer unit,
20 i.e. G_1 =solubilizing and/or reactive side group, and
 $G_2=G_3=G_4$ =H. Structures (1) and (2) are meant to imply both
homopolymers and copolymers where not all monomer units
have the same set of G 's.

Depending on relative reactivity of the reactive side
25 groups, the number of reactive side groups, the
concentrations of flexible polymer or monomer and
macromonomer, and the like, various structures of rigid-
rod reinforced polymeric composition will be obtained.
At one extreme, the rigid rod macromonomer will form one
30 or more bonds at each monomer unit, so that many reactive
groups per rigid rod chain are used, and many crosslinks
are made between the rigid rod macromonomer and flexible
polymer. Such highly crosslinked structures will be most
useful as thermosets and should be processed accordingly
35 (the majority of the crosslinks should be made after the
material has been shaped or formed; i.e., macromonomers
and flexible monomers are reacted in a mold or applied as

1 a coating and then cured; macromonomers, flexible polymers
and a catalyst are mixed, shaped and cured; etc.)

At the other extreme, only a few reactive side groups
per macromonomer chain are available to form crosslinks,
5 and a thermoplastic structure resembling a graft copolymer
results. In one embodiment, each rigid-rod chain has many
reactive side groups, but their reactivity is low under
a predetermined set of conditions, and only some of the
reactive groups participate in crosslinking, the rest
10 remain unreacted. In another embodiment, in addition to
macromonomers and a flexible polymer, a third component
is added, which third component will cap some of the
reactive groups, rendering them inert. This approach is
useful for tailoring one type of macromonomer for
15 different applications requiring different degrees of
crosslinking. In another embodiment, each macromonomer
chain has only a few reactive side groups, the rest being
inert under processing conditions.

It will be recognized by one skilled in the art that
20 a particular side group may be inert in one circumstance
and reactive in another. For example, an amide side group
may be reactive under conditions of transamidation, and
able to form covalent bonds with flexible polyamides, but
inert toward non-amide polymers such as polystyrene or
25 polyvinylchloride.

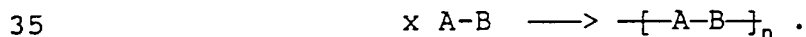
The macromonomers of the present invention may
interact differently with different classes of flexible
polymers, for example, addition polymers and condensation
polymers. A non-limiting list of flexible polymers that
30 can incorporate the macromonomers of the present invention
includes polyacetals, polyamides, polyimides, polyesters,
polycarbonates, polyamide-imides, polyamide-esters,
polyamide ethers, polycarbonate-esters, polyamide-ethers,
polyacrylates; elastomers such as polybutadiene,
35 copolymers of butadiene with one or more other monomers,
butadiene-acrylonitrile rubber, styrene-butadiene rubber,
polyisoprene, copolymers of isoprene with one or more

1 other monomers, polyphosphazenes, natural rubber, blends
 of natural and synthetic rubber, polydimethylsiloxane,
 copolymers containing the dimethylsiloxane unit,
 polydiphenylsiloxane, copolymers containing the
 5 diphenylsiloxane unit; polyalkylmethacrylates,
 polyethylene, polypropylene, polyphenylene oxide,
 polyphenylene sulfide, polystyrene, polyvinylacetate,
 polyvinylalcohol, and polyvinylchloride.

10 Reinforcing Condensation Polymers

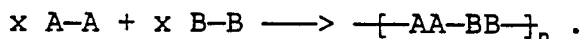
Rigid segments may be introduced into a wide variety
 of condensation polymers through the use of the rigid-rod
 macromonomers of the present invention. In one
 embodiment, the macromonomer is added during the polymer-
 15 forming reaction (polymerization) of the polymer to be
 stiffened. The polymer to be stiffened and/or
 strengthened will be referred to as the flexible polymer,
 regardless of its absolute stiffness. In one embodiment,
 in addition to being rigid, the macromonomer will dissolve
 20 in the flexible polymer polymerization dope and have
 functionality enabling it to take part in the
 polymerization reaction. In another embodiment, the
 initially formed flexible condensation polymer is
 isolated, and a solvent is selected for both the
 25 macromonomer and the flexible polymer. The flexible
 polymer and macromonomer are redissolved, and the
 macromonomer reacts with the originally formed flexible
 polymer. Macromonomers may also be dissolved in the melt
 of the flexible polymer, where reaction of the side groups
 30 may then occur.

Several types of condensation polymers may be
 distinguished. Condensation polymers may include a single
 monomer, usually referred to as an A-B monomer:



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1 Alternatively, two complementary difunctional
monomers, usually referred to as A-A and B-B may be
condensed:



5

Where the rigid-rod macromonomers are used in a
condensation polymerization, the reactive side groups can
be considered to be the A-, or B- type end groups
typically described in A-A, A-B, and B-B monomers used in
10 condensation polymerization systems. A-A, B-B, and A-B
type monomers are described in U.S. Patent No. 4,000,187
to Stille, incorporated herein by this reference.

Non-limiting examples of A-A and B-B type monomers
include diamine-type monomers such as p-phenylenediamine,
15 m-phenylenediamine, oxydianiline, methylenedianiline,
tetramethylenediamine, hexamethylenediamine, and the like;
diol-type monomers such as resorcinol and hexanediol;
bisaminoketones, bisthiols, and the like; diacid-type
monomers such as adipic acid, adipoyl chloride, esters of
20 adipic acid, terephthalic acid, terephthaloyl chloride,
esters of terephthalic acid, bisectomethylenes,
bis(activated halides) such as chlorophenyl sulfone, and
the like.

Non-limiting examples of A-B type monomers include
25 amino acids, amino acid esters, activated halides such as
4-fluoro-4'-hydroxybenzophenone, lactams (e.g.,
caprolactam), lactones, and the like.

Several types of reinforced polymers and copolymers
are possible with the rigid-rod macromonomers of the
present invention. One skilled in the art will appreciate
30 that the backbone of the macromonomers of the present
invention, generally designated "M", can have A-type,
B-type or both A- and B-type reactive side groups pendant
therefrom. In other words, a given macromonomer can have
35 reactive side groups that are complementary to A-type,
B-type, and/or both A- and B-type condensation monomers.

1 Macromonomers having "A" type reactive side groups,
complementary to B-B and A-B type condensation monomers,
may be used in the following exemplary, and non-limiting,
ways:

5

(a) Macromonomer + AA or BB $\rightarrow$ crosslinked polymer
with short chains between crosslinks (Fig. 1);

10

(b) Macromonomer + AA + BB $\rightarrow$ crosslinked polymer
with long chains between crosslinks; chain
length between crosslinks is dependent on the
amounts of A-A and B-B monomers (Fig. 2);

15

(c) Macromonomer + AB $\rightarrow$ flexible polymer chains
grafted to rigid-rod segments (Fig. 3);

20

(d) Macromonomers + AA + BB + preformed flexible
polymer $\rightarrow$ semi-interpenetrating network of
uncrosslinked flexible polymer in a crosslinked
macromonomer - AA - BB network
(Fig. 4).

25

Order of addition and control of monomer imbalance
can be used to create complex, crosslinked polymeric
compositions. Any set of A-A, B-B and A-B monomers which
will co-condense with the macromonomers of the present
invention will be called complementary monomers. For
example, terephthalic acid and ethylene glycol are
complementary monomers that will condense with rigid-rod
macromonomers having A-type reactive side groups (for
example hydroxyalkyl or carboxylate side groups).
Similarly, a co-polyester can be formed by condensing A-
type macromonomers having structure (1) or (2) with one
or more complementary monomers such as biscarboxylic
acids, biscarboxylic acid halides, biscarboxylic acid
esters, bisdiols, hydroxycarboxylic acids, lactones, and
the like.

35

1 Three variables which may be used to control the
properties of the copolymers prepared by incorporating the
macromonomers of the present invention are: the average
length of the rigid segments, L_r , which is proportional to
5 DP_n , the average number of reactive side groups per
macromonomer, and the weight fraction of rigid segments
in the copolymer, W_r .

Reinforcing Thermoset Resins

10 The rigid-rod macromonomers of the present invention
may also be used to form thermoset resins, either alone
or in conjunction with existing thermoset formulas to
impart strength, stiffness, and/or a lower coefficient of
thermal expansion. Thermosets are often formed in stages,
15 where monomers are allowed to react to a limited extent
to give a processable resin, which is cured in a second
stage, often by heat treatment. Thermosets formed in
accordance with the present invention are typically highly
crosslinked, and the stages are defined by the degree of
20 crosslinking. Aside from the insoluble, infusible nature
of the resulting cured thermoset, the chemistry is similar
to condensation polymers.

 It will often be desirable to use the rigid-rod
macromonomers of the present invention with other small
25 molecule crosslinkers, curing agents, additives, fillers,
modifiers and the like. Diols, polyols, diamines and
polyamines are commonly used thermoset precursors that
will react with the macromonomers of the present
invention. A non-limiting example of the use of such
30 compounds is the formation of a two part thermosetting
resin, wherein Part 1 is primarily comprised of a rigid-
rod macromonomer, and Part 2 is primarily comprised of a
curing agent such as a diamine, or a catalyst. Two part
resins often have longer shelf lives, because each
35 component alone is relatively unreactive.

 Rigid-rod polymers heretofore have not been used in
thermosets, primarily because it is commonly thought that

1 rigid-rod polymers are not soluble in resin systems,
including solutions of resins or pre-polymers used to
prepare thermoset resins. The rigid-rod macromonomers of
this invention, however, are soluble in common solvents
5 and can be made compatible with various resin systems by
proper choice of solubilizing side groups. The reactive
side groups also should be compatible with the cure
chemistry of the thermoset.

Typically, but not necessarily, the reactive side
10 groups will be chosen to match the reactive groups in the
thermoset. For example, reactive side groups should be
epoxy groups, phenol groups, or amino groups for use with
an epoxy resin, or phenol groups for use with phenolic
resins. It is also usually desirable for the cure
15 temperatures of the reactive side groups and the thermoset
to be similar. Non-limiting examples of thermoset systems
which can incorporate the rigid-rod macromonomers of the
present invention are: allyl resins,
benzophenonetetracarboxylic acid or its anhydride,
20 bisacetylene resins, bisbenzocyclobutene resins,
bisbiphenylene resins, bisphenoltetracarboxylic acid, or
its anhydride, diepoxides, epoxy resins, formaldehyde,
paraformaldehyde, paraformaldehyde-based resins, furan
resins, phenolic resins, polyepoxides, trioxanes,
25 phenol-formaldehyde resins, novolac resins, resole resins,
resorcinol-formaldehyde resins, silicone resins,
urethanes, melamine resins, isocyanate resins, resins
based on cyanuric acid and cyanuric chloride, polyamic
acids, polyamide resins, crosslinked polyamides and
30 polyesters, unsaturated polyester resins, urea resins,
vinyl ester resins, and natural resins, gums, lacquers and
varnishes.

The rigid-rod macromonomers of the present invention
may also be used alone to form thermosetting resins. In
35 this case, the side groups G are not needed for solubility
in, or compatibility with, other resins, polymers or
monomers, but impart some degree of thermoformability.

1 In general, rigid-rod macromonomers with a lower degree
of polymerization, smaller n will have lower glass
transition temperatures and melting temperatures and will
be more readily heat processed. As is known in the art
5 it is necessary to adjust the melting temperature and cure
temperature so that the polymer system does not cure
before it is thermoformed, and so that unreasonably high
temperatures are not needed for curing.

When used as a thermoset, the rigid-rod macromonomer
10 must have sufficient flow properties to be shaped or
processed, typically at elevated temperatures. Thus, the
side groups G and the DP_n are chosen to allow some degree
of thermoformability. In general, larger and more
flexible G 's increase processability, as does lower DP_n .
15 On the other hand, smaller G 's and larger DP_n 's enhance
stiffness and strength, so that optimum sizes for DP_n and
 G can be found. Different processing methods will have
different requirements; for example, sintering does not
require complete melting, whereas injection molding
20 requires low viscosity melts. The reactive side groups
of a rigid-rod macromonomer used as a thermoset should
have a cure temperature consistent with the required
processing temperature. If the cure temperature is too
low, the material will cure before processing can be
25 completed. If the cure temperature is too high, the
material may not fully cure or the flow properties at the
curing temperature may be undesirable. In an exemplary
and non-limiting embodiment of the invention, cure is
effected by using a curing agent such as a catalyst or
30 low molecular weight crosslinking agent.

Non-limiting examples of reactive side groups with
good cure temperatures are maleimides, nadimides, and
acetylenes.

35 Reinforcing Addition Polymers

The rigid-rod macromonomers of the present invention
also find use as pre- and post-polymerization additives.

1 As post-polymerization additives, rigid-rod macromonomers
may be used in compounding, blending, alloying, or
otherwise mixing with preformed polymers, preformed
5 blends, alloys, or mixtures of polymers. In these cases
the solubilizing side groups and/or reactive side groups
help make the macromonomer compatible with the polymer to
be reinforced. Such compounding, blending, alloying etc.
may be done by solution methods, melt processing, milling,
10 calendering, grinding or other physical or mechanical
methods, or by a combination of such methods. Chemical
reaction of the reactive side groups of the macromonomer
with the polymer into which the macromonomer is being
incorporated may take place during such processes, or the
15 reactive side group may simply serve to make the rigid
segment M compatible with the preformed polymer, for
example via non-covalent interactions including hydrogen
bonding, ionic bonding and van der Waals forces.
Mechanical heating or shearing can initiate such chemical
processes which will effect the final composition.

20 For many addition polymers, where it is not
convenient to introduce the macromonomer during
polymerization, the rigid-rod macromonomer may be
introduced by the above methods in post-polymerization
processes. Non-limiting examples of such polymers
25 include, polyethylene, polypropylene, polyvinylchloride,
polystyrene, polyacrylonitrile, polyacrylates,
acrylonitrile-butadiene-styrene (ABS), styrene butadiene
rubber (SBR), and other homopolymers, copolymers, blends,
alloys etc. A macromonomer having reactive side groups
30 that act as initiators for addition polymerization can be
used to prepare graft copolymers having a rigid-rod main
chain and flexible side chains (Fig. 5).

35 A macromonomer having reactive side groups that act
as addition type monomers, for example styrene side
groups, may be used to form addition polymers having
rigid-rod segments (Fig. 6). Depending on concentrations

1 and reactivity of reactants, the resulting addition polymers will exhibit varying degrees of crosslinking.

The rigid rod macromonomers of the present invention may be used in any of the various types of polymerization processes, including but not limited to, bulk polymerization, suspension polymerization, emulsion polymerization, reaction injection molding, reinforced reaction injection molding, resin transfer molding and the like.

10 Other applications will be apparent to those skilled in the art.

As pre-polymerization additives, the macromonomers of the present invention are added along with other monomers to be polymerized to yield the final polymer.

15 Optionally, conventional fillers such as carbon black, silica, talc, powders, chopped or continuous fibers, or other macroscopic reinforcing agents as are known in the art can be added to the polymer systems which incorporate the rigid-rod macromonomers of the present invention. In embodiments of the invention in which
20 macroscopic reinforcing agents are added, the macromonomers of the present invention add additional strength, stiffness, creep resistance, fire resistance toughness and/or other properties to what would otherwise
25 be conventional composites and resins and also serve to decrease the amount of filler used in a conventional composite or resin.

The rigid rod macromonomers of the present invention may be used to enhance the properties of all types of natural and synthetic polymers, including but not limited
30 to, addition polymers, condensation polymers, ring opening polymers, thermosets, thermoplastics, elastomers, rubbers, silicones, silicone rubbers, latexes, gums, varnishes, and cellulose derived polymers.

35 When used with rubbers and elastomers having a polymer network the rigid rod macromonomers act to modify such properties as strength, abrasion resistance,

1 resilience, wear resistance, creep and the like, and may
be used to replace or eliminate the use of fillers.

The reinforced polymers of the present invention may
be used to fabricate films, fibers, and molded parts
5 having improved properties, especially improved mechanical
properties, relative to the same material without
reinforcement by rigid-rod macromonomers. Other non-
limiting examples of applications of the reinforced
polymers of the present invention include adhesives,
10 elastomers, coatings, membranes, plastic sheet, and sheet
molding compounds.

The reinforced polymers of the present invention may
contain in addition to rigid-rod segments conventional
additives, including but not limited to, plasticizers,
15 flame retardants, smoke suppressants, fillers, additional
polymers, compatibilizers, lubricants, surface modifiers,
antioxidants, dyes and pigments, surfactants,
biodegradability enhancers, biomodifiers, UV absorbers and
the like.

20

Methods for Preparing Macromonomers Having Reactive Side Groups

In order to introduce rigid segments into a wide
variety of polymers, polymeric compositions, ceramics,
25 glasses, and the like, a rigid-rod type macromonomer is
first prepared. The poly-1,4-phenylene structure (1) and
aza derivatives (structure (2)) offer a stiff, strong,
thermally stable, and chemically inert backbone, of
potentially low cost. Pendent side groups impart
30 solubility and reactivity to the macromonomer.

Several methods may be used to prepare substituted
poly-para-phenylenes and aza analogs. The simplest rely
on reductive condensation of 1,4-dihaloaromatics, either
by way of a Grignard reagent, or directly. A catalyst,
35 such as bis(triphenylphosphine) nickel (II) chloride or
1,4-dichloro-2-butene is used. Para-bromoaryl boronic
acids may be coupled using palladium based catalysts.

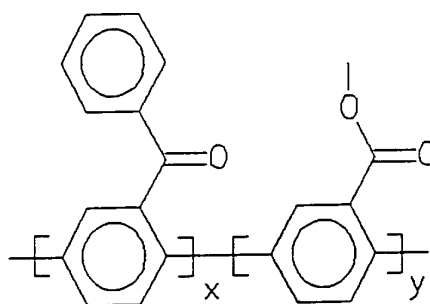
1 Polyphenylenes have also been prepared by methods which
do not give exclusive para linkage, such as Diels-Alder
condensation of bis-acetylenes and bis-pyrones,
polymerization of 1,3-cyclohexadiene followed by
5 aromatization and oxidative polymerization of benzene.

If the macromonomer is prepared using a transition
metal catalyst, and the synthesis proceeds through
metallo-terminated chains as intermediates, the molecular
weight of the resulting macromonomer may be controlled by
10 the catalyst-to-monomer ratio. In this case the
polymerization will cease when the number of chain ends
(capped with catalyst) equals the number of catalyst
molecules initially present. The DP_n will equal twice the
monomer to catalyst ratio. End groups (not shown in the
15 structures provided herein) then may be introduced by
adding reagents which displace the metallo end groups.
For example, if the macromonomer is worked-up in an
alcohol, the metal groups terminating the chains of the
macromonomer are displaced by protons (H). The
20 metallo-terminated macromonomer is thereby quenched.

Macromonomers of the present invention may have, in
addition to reactive side groups, reactive end groups.
Macromonomers having reactive end groups may be prepared,
for example, by adding endcappers during the coupling
25 reaction, or by displacing the metallo end groups with an
endcapper. The endcappers may themselves be reactive
groups or protected forms of reactive groups.

The rigid-rod macromonomers of the present invention
may be made by these and other methods, keeping in mind
30 the special requirements of solubilizing and reactive side
groups. The catalytic reductive coupling of
1,4-dihaloaryls is preferred, (and more preferably,
reductive coupling of 1,4-dichloroaryls) because of its
simplicity and wider tolerance of functional groups. The
35 special nature of the rigid-rod macromonomers of the
present invention must be taken into account in order to
successfully prepare these macromonomers.

1 Rigid-rod macromonomers comprised of both monomer
units bearing solubilizing side groups and monomer units
bearing reactive side groups are conveniently prepared by
either of two different routes. One approach is to
5 copolymerize two or more different monomers, at least one
of which bears one or more reactive side groups. A non-
limiting example is copolymerization of a 19:1 molar ratio
of 2,5-dichlorobenzophenone and methyl-2,5-dichloro-
benzoate to yield a macromonomer having a structure (4):



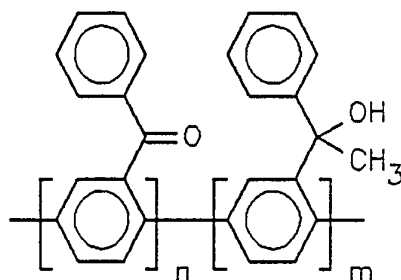
(4)

20 where $x \approx 95\%$, $y \approx 5\%$, and the monomer units bearing a
reactive ester group are randomly distributed amongst the
monomer units bearing a solubilizing benzoyl group.

A second approach is to first prepare a homopolymer
and then react an excess of said homopolymer with a
predetermined amount of a reagent to yield a partially
25 modified polymer that is, in effect, a copolymer. A non-
limiting example is polymerization of 2,5-dichloro-
benzophenone to yield parapolybenzoylphenylene, followed
by treatment with a predetermined amount of methyl
30 lithium, followed by hydrolysis to yield a macromonomer
having the structure (5):

1

5

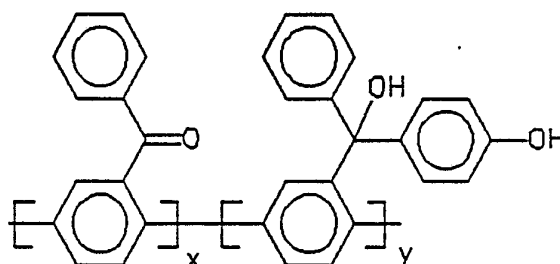


(5)

10 where $n + m = 100\%$, and the monomer units bearing a reactive benzylhydroxy side group are randomly distributed amongst the monomer units bearing a solubilizing benzoyl group.

15 A second non-limiting example of side chain modification is the treatment of parapolybenzoylphenylene with a predetermined amount of phenol in the presence of a Lewis acid catalyst to give a macromonomer having the structure (6):

20



25

where $x + y = 100\%$, and the monomer units bearing a reactive (and solubilizing) phenolic side group are randomly distributed amongst the monomer units bearing a solubilizing benzoyl group.

30

The synthesis of even short rigid-rod molecules is made difficult by their low solubility. For example, poly-1,4-phenylene (structure (1), where G_1 through G_4 and E are each hydrogen) compounds with n greater than about
 35 8 are essentially insoluble in all solvents and are infusible. Solubility is achieved in the present invention by appropriate choice of side groups G , bearing

1 in mind the solvent systems to be employed. For example,
for polar aprotic solvents, such as dimethylformamide or
N-methylpyrrolidone, polar aprotic side groups such as
amides and ketones are appropriate. For protic solvents,
5 e.g. water, acids or alcohols, ionizable side groups, e.g.
pyridyl or sulfonate, might be considered.

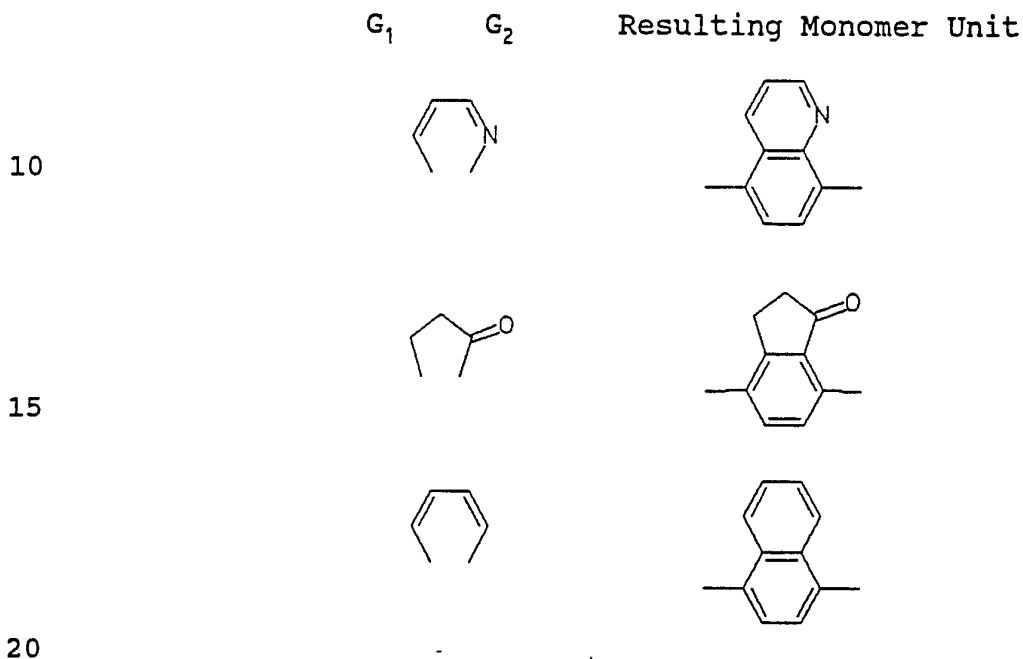
The side groups may also act to twist the main chain
phenylene units out of planarity (although the main chain
remains straight and not coiled). Phenylene pairs with
10 substituents at the 2,2' positions will be twisted out of
planarity by steric repulsion. Since planar phenylene
chains pack more efficiently, a twisted chain will be more
soluble. One means of solubilizing rigid-rod molecules
is to provide adjacent phenylene pairs with substituents
15 ortho with respect to the other phenylene of the pair.
Even occasional 2,2' side groups will disrupt packing and
enhance solubility. Another means of improving solubility
is to decrease the order (increase the entropy) of the
side groups, for example by a random copolymer with two
20 or more different types of substituents. Other mechanisms
of increasing solubility may also be possible.

Non-limiting examples of solubilizing side groups
are: phenyl, biphenyl, naphthyl, phenanthryl,
anthracenyl, benzyl, benzoyl, naphthoyl, phenoxy,
25 phenoxyphenyl, phenoxybenzoyl, alkyl, alkyl ketone, aryl,
aryl ketone, aralkyl, alkaryl, alkoxy, aryloxy, alkyl
ester, aryl ester (esters may be C-bound or O-bound),
amide, alkyl amide, dialkyl amide, aryl amide, diaryl
amide, alkyl aryl amide, amides of cyclic amines such as
30 piperidine, piperazine and morpholine (amides may be CO-
bound or N-bound), alkyl ether, aryl ether, alkyl
sulfides, aryl sulfides, alkyl sulfones, aryl sulfones,
thioethers, fluoro, trifluoromethyl, perfluoroalkyl, and
pyridyl, where alkyl is a linear or branched hydrocarbon
35 chain having between 1 and 30 carbon atoms, and aryl is
any single, multiple or fused ring aromatic or
heteroaromatic group having between 3 and 30 carbon atoms.

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1 Fluorine-substituted analogs of the above-identified side groups may also be used.

5 G_1 and G_2 , and/or G_3 and G_4 may be interconnected to form bridging groups. Non-limiting examples of such groups and the monomer units that result are shown below:



20 Solubilizing side groups G may also be oligomeric or polymeric groups. Using side groups which are functionally equivalent to the flexible polymer to be strengthened increases the compatibility of the rigid segments with the flexible segments. A non-limiting example is the use of a macromonomer denoted " M_{oligo} ," bearing oligocaprolactam side groups G , as a comonomer with caprolactam in the preparation of poly(hexamethylenedipamide-co- M_{oligo}).

30 For cases where the monomer unit of the macromonomer is unsymmetrical about the plane perpendicular to the polymer axis and centered on the monomer unit, for example if G_1 is benzoyl and G_2 , G_3 , and G_4 , are hydrogen, isomeric forms of the macromonomer exist. The monomers can link exclusively head-to-tail to form a regular structure. The monomers can also form a regular structure by linking exclusively head-to-head and tail-to-tail. Other more

1 complicated structures and a random structure are also
possible. The particular monomers and conditions used to
form the macromonomer will determine the detailed
structure. As used herein, structures (1), (2) and (3)
5 represent all isomeric cases, either regular or random.
Similarly, macromonomers of the type depicted in
structures (4)-(6) are not limited to the particular
isomers shown therein.

It will sometimes be desirable to include 1,4-
10 dichlorobenzene as a comonomer, so that some monomer units
will be unsubstituted, i.e., $G_1 = G_2 = G_3 = G_4 = H$. The
unsubstituted units will lower cost, but may also lower
solubility.

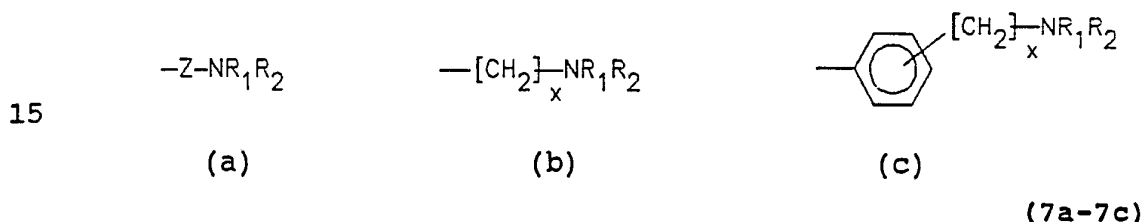
15 Reactive Side Groups

The reactive side groups, G, are chosen to allow
chemical interaction with the flexible polymer or
inorganic matrix to be stiffened or strengthened.

Reactive side groups can be further derivatized to
20 provide additional functionality, as for example during
deprotection, or transformation of one reactive group into
another, for example reduction of a nitrile into an amine,
an aldehyde into an alcohol, or conversion of an amine
into an imine. More than one type of reactive side group
25 may be present.

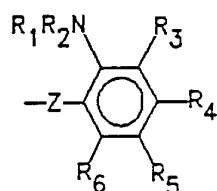
Amines form an important class of reactive side
groups. Amine-functionalized macromonomers can be used
with polyamides, polyimides, polyimidamides, polyureas,
polyimines, and other polymers derived from bisamine
30 monomers. Amine-functionalized macromonomers can also be
used with polymers not derived from bisamine monomers,
such as epoxides and polyesters; in the latter case the
macromonomer would be incorporated into the polyester
chain via amide links. Preparation of the amine-
35 functionalized macromonomers can involve protection/
deprotection of the amine groups, for example as a
succinimide or an amide.

1 The following are non-limiting examples of amine
 derived reactive side groups: amino, aminoalkyl,
 aminoaryl, aminoalkaryl, aminoaralkyl, aniline, C-
 5 alkylaniline, N-alkylaniline, aminophenoxy, and
 aminobenzoyl. Other substituted and/or chemically
 protected aniline side groups may also be used. The
 following structures illustrate non-limiting examples of
 amine-derived reactive side groups. Typical amines, amino
 10 alkyls, and amino aralkyls are given by the following
 structures (7a-7c):

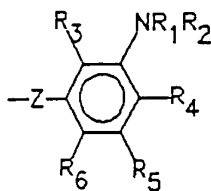


20 where R_1 and R_2 may be independently chosen from:
 hydrogen, alkyl, aryl, alkaryl, aralkyl, alkylketone,
 arylketone, alkylether or aryether, where alkyl and aryl
 are as defined above, x ranges from one to about twenty,
 25 and Z is a difunctional group chosen from: nil,
 phenyleneoxy, ketophenylene, phenylenesulfone, $-O-$, $-NH-$,
 keto, $-SO_2-$, aryl, alkyl, alkaryl, or aralkyl. R_1 and R_2
 include bridging groups, such as $-CH_2CH_2CH_2CH_2CH_2-$,
 $-CH_2CH_2OCH_2CH_2-$, and $-CH_2CH_2CH_2CO-$. R_1 and R_2 will often be
 30 used as protecting groups, to be removed at a later stage
 of processing, and as such include common amine and
 alcohol protecting groups, non-limiting examples of which
 are: trimethylsilyl, trityl, tetrahydropyranyl, tosyl,
 methoxyisopropylidene, imide, imine, amide, ester, and the
 35 like.

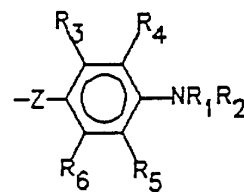
Typical amino aryl reactive side groups, G, have the structures (8a-8c):



(a)



(b)

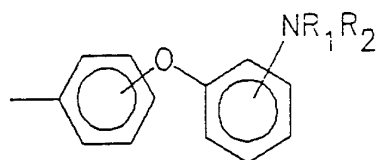


(c)

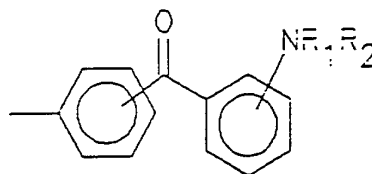
(8a-8c)

where Z, R₁ and R₂ are as defined above, and R₃ - R₆ are selected from the same group as R₁ and R₂. Aniline side groups have the above structure where Z is nil and the R's are all hydrogen.

Aminophenoxyphenyl and aminobenzophenone side groups have the general structures (9a and 9b):



(a)



(b)

(9a-9b)

where R₁ and R₂ are as defined above.

Imides comprise a second class of reactive side groups. The maleimides are represented by the structures 7a-9b, where R₁ and R₂ together equal the bridging group -COCH=CHCO-. Bismaleimides are commercially valuable in thermoset resins. Rigid-rod macromonomers with maleimide end groups are useful for strengthening conventional bismaleimide resins. They may also be used alone as novel

-35-

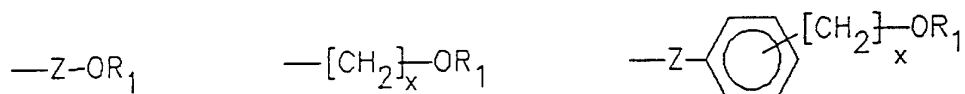
1 bismaleimide resins containing rigid-rod elements. Other
reactive imide end groups are contemplated by the present
invention, including the nadimide end groups. Unreactive
imides may also be used; succinimide may be used as a
5 protected form of amine.

Closely related to the amines are the amides. In
structures 7a-9b, if R_1 or $R_2 = -COalkyl$ or $-COaryl$, the
reactive side groups are amides. If R_1 or $R_2 = -COCH=CH_2$,
the reactive side groups are acrylamides. Amide-
10 functionalized macromonomers are also useful in
reinforcing polyamides, such as nylon. Amide groups may
react by transamination with the flexible polymer during
polymerization or compounding.

Another important class of reactive side groups are
15 alcohols and ethers. Diol-functionalized macromonomers
may be used as comonomers with other diol monomers.
Polyesters, polycarbonates, urethanes, and polyethers are
non-limiting examples of polymers prepared from diols.
Alcohol macromonomers may also be used in non-diol derived
20 polymers, for example, polyamides, where linkage to the
macromonomer is through ester links. Both the amine
macromonomers and the alcohol macromonomers may be used
to replace dibasic monomers, in general, in condensation
polymerizations.

25 Non-limiting examples of alcohol-functionalized
macromonomers are: hydroxy, hydroxyalkyl, hydroxyaryl,
hydroxyalkaryl, hydroxyaralkyl, phenol, C-alkylphenol, O-
alkylphenol, hydroxyphenoxy, and hydroxybenzoyl. The
following non-limiting structures (10a-10c) illustrate
30 exemplary alcohol side groups:

1



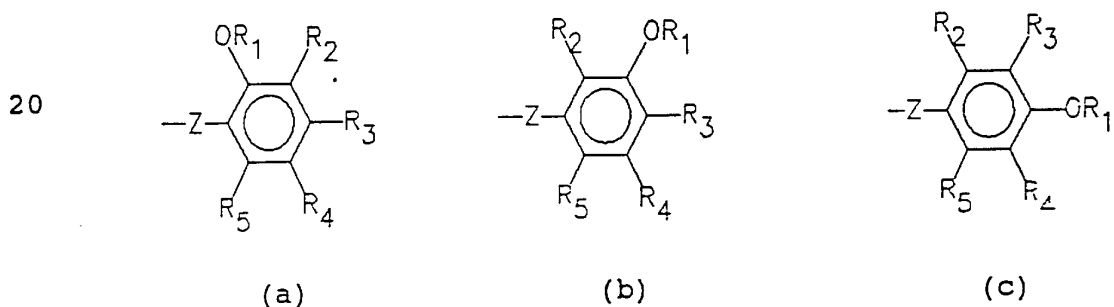
5

(a) (b) (c)
(10a-10c)

where R_1 , x and Z are as defined in the discussion following structures (7a-7c).

15

The following structures (11a-11c) are representative of phenolic side groups:



20

(a)

(b)

(c)

25

(11a-11c)

where $R_1 - R_6$, and Z are as defined above.

The following structures (12a-12c) are more specific examples of the above structures:

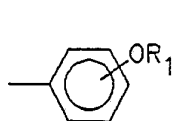
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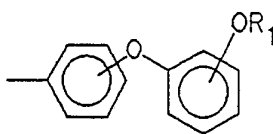
-37-

1

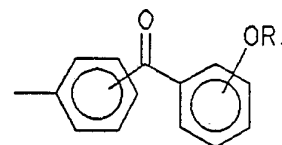
5



(a)



(b)



(c)

(12a-12c)

10

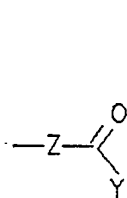
where R_1 is as defined above.

For $R_1=H$, the structures (12a-12c) represent phenol, hydroxyphenoxyphenyl, and hydroxybenzophenone side groups, respectively. For R_1 =ketoalkyl or ketoaryl, the structures (12a-12c) are phenylesters. R_1 may contain additional reactive groups, such as acrylate or vinyl. In structures 9a through 11c, for $R_1 = -COCH=CH_2$ the reactive side groups are acrylates, for $R_1 = -CH=CH_2$ the reactive side groups are vinyl ethers.

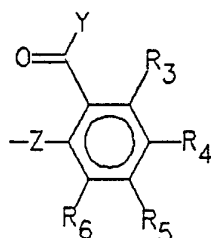
Carbonyl-containing reactive side groups including acetyl, formyl, carboxy, ester, amide, acrylate, ketoalkyl and ketoaryl are represented by the structures (12a-12d) where Y is CH_3 , H, OH, OR_1 , NR_1R_2 , vinyl, alkyl and aryl respectively, and $R_1 - R_6$ and Z are as defined above.

Amides may be C or N bound; see structures 6a-8b above.

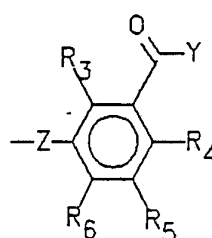
30



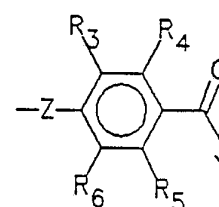
(a)



(b)



(c)



(d)

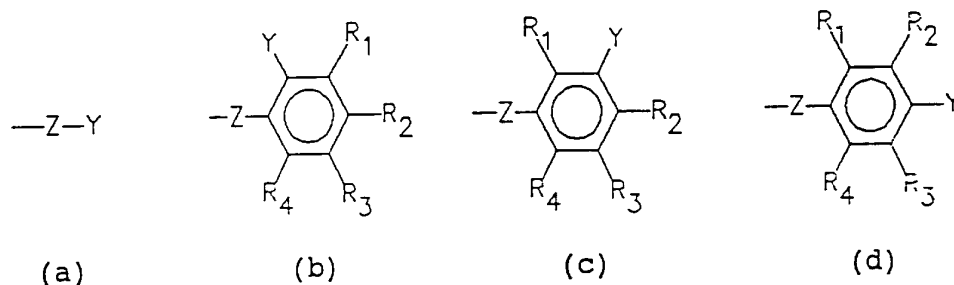
35

(13a-13d)

1 Macromonomers of the present invention having carboxy side groups may be used to reinforce polyesters and polyamides.

5 Acetylene side groups have the structures (14a-14d) where Y is -CCH. Olefin side groups have the structures (14a-14d) where Y is -CH=CH₂. Halide, cyano, cyanate, and isocyanate side groups have the structures (14a-14d) where Y is -halogen, -CN, -OCN and -NCO respectively.

10



(14a-14d)

20 Reactive side groups may also be strained ring compounds including epoxides, biphenylenes and benzocyclobutenes.

25 In situations where the reactive side groups G are reactive with each other, both the reactive side groups G and the groups on the flexible polymer or monomer with which they are ultimately to react should be selected so that the relative rates of reaction are approximately equal. This will enhance the randomness of the distribution of the macromonomer within the final polymer.

30 When the rigid-rod macromonomers of the present invention are used as pre-polymerization additives, they are preferably added in an amount such that W_r ranges from 1 percent to 60 percent, i.e., the rigid-rod macromonomers make up from 1 percent to 60 percent of the weight of the resulting polymeric material. Such a range takes into account the trade off between increased cost and decreased processibility that results as the value of W_r increases

35

1 in magnitude. In practice, it is desirable to
experimentally determine the optimal weight fraction
required for particular applications.

5 In certain circumstances, it may be desirable for W_r
to exceed 60 percent of the total weight of the
copolymeric material. For instance, when the rigid-rod
macromonomers of the present invention are used alone as
thermosetting resins, W_r can approach the limiting value
of 100 percent, depending on the size, frequency, and
10 orientation of the crosslinking groups formed during
curing.

There will also be an optimal range for L_r , typically
between 8 and 500 repeat units, beyond which additional
increases in length will have little further effect on
15 strength or stiffness but will reduce processibility.
Optimal ranges for both W_r and L_r can be readily
determined by one skilled in the art.

The aspect ratio of the macromonomers incorporated
into copolymers also affects the physical properties of
20 the copolymers, particularly the processibility thereof.
The aspect ratio of a macromonomer is defined to be the
length to diameter ratio of the smallest diameter cylinder
which will enclose the macromonomer segment, including
half the length of the terminal connecting bonds,
25 including hydrogen but not any other attached side groups,
such that the axis of the cylinder is parallel to the
connecting bonds in the straight segment.

For rigid-rod polyphenylenes, and aza analogs, the
aspect ratio is approximately equal to the DP_n , because
30 the phenylene monomer unit has an aspect ratio of about
one.

When the average aspect ratio of the macromonomers
is less than about 7 or 8, the macromonomers typically do
not impart the desired strength and stiffness into the
35 final polymer. As the aspect ratio is increased, the
mechanical properties of the reinforced polymer improve.
All other factors being equal, a longer rigid segment will

1 provide a greater increase in stiffness than a shorter
rigid segment. This is true for reinforcement of any
geometrical type of polymer, e.g., linear, branched,
5 crosslinked, and the like. It is known in the art that
for conventional fiber-containing composites mechanical
properties improve rapidly up to aspect ratios of about
100, after which there are lesser improvements. A similar
situation has been found to exist for rigid-rod
macromonomers.

10 Although mechanical properties of the polymers
improve as the aspect ratio increases, processing becomes
more difficult. Viscosities of polymer solutions are
dependent on the DP_n of the polymer. Viscosities of
rigid-rod polymers increase much more rapidly with DP_n
15 than viscosities of flexible polymers. Similarly, melt
viscosities of flexible polymers reinforced with rigid-rod
polymers increase with the DP_n of the rigid segments,
making thermal processing more difficult as DP_n increases.

There is generally a trade-off between improved
20 mechanical properties and difficulty of processing,
resulting in an optimal aspect ratio and DP_n for the
rigid-rod macromonomers. For example, if it is desired
to increase the modulus of a flexible polymer reinforced
with rigid-rod macromonomers, the aspect ratio of the
25 macromonomer could be increased, but the melt and solution
viscosity will increase and solubility of the rigid-rod
macromonomer will decrease, making processing and
preparation more difficult. DP_n 's of about 100 are often
optimal; however, higher or lower DP_n 's may sometimes be
30 desirable.

SYNTHETIC METHODS

The following synthetic procedures are exemplary
35 methods that may be used in the preparation of precursors
to, and reagents used in the synthesis of, the rigid-rod
macromonomers of the present invention; an exemplary

1 method of preparing succinimide-protected amines; and a
method for deprotecting protected side groups. The
choices and amounts of reagents, temperatures, reaction
times, and other parameters are illustrative but are not
5 considered limiting in any way. Other approaches are
contemplated by, and within the scope of, the present
invention.

Preparation of 2,5-Dichlorobenzoyl Compounds

10 2,5-dichlorobenzoyl-containing compounds (e.g. 2,5-
dichlorobenzophenones and 2,5-dichlorobenzamides) can be
readily prepared from 2,5 dichlorobenzoylchloride. Pure
2,5-dichlorobenzoylchloride is obtained by vacuum
distillation of the mixture obtained from the reaction of
15 commercially available 2,5-dichlorobenzoic acid with a
slight excess of thionyl chloride in refluxing toluene.
2,5-dichlorobenzophenones (2,5-dichlorobenzophenone, 2,5-
dichloro-4'-methylbenzophenone, 2,5-dichloro-4'-
methoxybenzophenone, and 2,5-dichloro-4'-
20 phenoxybenzophenone) are prepared by the Friedel-Crafts
benzoylations of benzene and substituted benzenes (e.g.
toluene, anisole, diphenyl ether, respectively), with 2,5-
dichlorobenzoylchloride at 0-5°C using 2-3 mole
equivalents of aluminum chloride as a catalyst. The solid
25 products obtained upon quenching with water are purified
by recrystallization from toluene/hexanes. 2,5-
dichlorobenzoylmorpholine and 2,5-
dichlorobenzoylpiperidine are prepared from the reaction
of 2,5-dichlorobenzoylchloride and either morpholine or
30 piperidine, respectively, in toluene with pyridine added
to trap the HCl that is evolved. After washing away the
pyridinium salt and any excess amine, the product is
crystallized from the toluene solution.

35 Preparation of Activated Zinc Powder

Activated zinc powder is obtained after 2-3 washings
of commercially available 325 mesh zinc dust with 1 molar

1 hydrochloric acid in diethyl ether (anhydrous) and drying
in vacuo or under inert atmosphere for several hours at
about 100-120°C. This material should be used immediately
or stored under an inert atmosphere away from oxygen and
5 moisture.

Preparation of Succinimide Protected Amines

The dry amine (0.5 mole) and succinic anhydride (0.5
mole) are dissolved in 2L dry toluene. Catalyst, p-
10 toluenesulfonic acid (0.01 mole), is then added and the
mixture is held at reflux for 24 hours, using a Dean-Stark
trap to collect water. After cooling, the product is
precipitated with diethyl ether, filtered, washed with
ether and dried.

15

Deprotection of Protected Side Groups

In the cases where the functional side groups are
protected as an imide, amide, or ester, the protecting
groups are removed as follows: The protected macromonomer
20 is suspended in 25 ml of 10% HCl in ethanol and heated to
reflux for six to twelve hours. This mixture is
neutralized with sodium hydroxide, filtered, washed and
dried. Further purification by dissolution and
precipitation by adding a non-solvent may be effected.

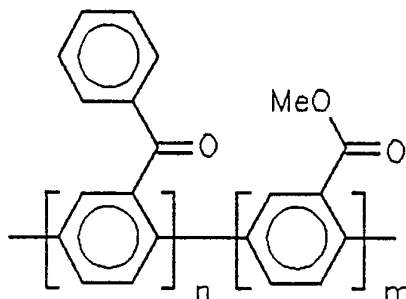
25 The following specific examples of preparing
rigid-rod macromonomers and polymers containing rigid-rod
macromonomers are illustrative of the present invention,
but are not considered limiting thereof in any way.

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EXAMPLE 1.

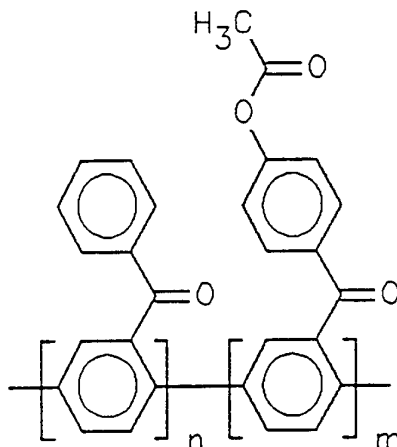
Preparation of a macromonomer of the structure:



Anhydrous bis(triphenylphosphine) nickel(II) chloride (0.25 g; 0.39 mmol), triphenylphosphine (0.60 g; 2.29 mmol), sodium iodide (0.175 g, 1.17 mmol) and 325 mesh activated zinc powder (1.2 g; 18.4 mmol) are placed into a flask under an inert atmosphere along with 7 ml of anhydrous N-methylpyrrolidinone (NMP). This mixture is stirred for about 10 minutes at room temperature, leading to a deep-red coloration. A solution of 2,5-dichlorobenzophenone monomer (3.26 g; 12.98 mmol) and of methyl-2,5-dichlorobenzoate comonomer (0.14 g; 0.68 mmol) in 8 ml of anhydrous NMP is then added by syringe. After stirring for about 12 hours at 50-60°C, the resulting viscous solution is poured into 100 ml of 1 molar hydrochloric acid in ethanol to dissolve the excess zinc metal and to precipitate the functionalized copolymer. This suspension is filtered and the precipitate triturated with acetone and dried to afford a light yellow to white powder. Approximately 5% of the sidechain appendages of the resulting rigid-rod copolymer contain reactive ester groups. Even greater reactivity may be imparted by hydrolyzing the ester groups to carboxy groups (e.g. by refluxing in 10% HCl in ethanol for six to twelve hours and then neutralizing with sodium hydroxide).

EXAMPLE 2.

Preparation of a macromonomer of the structure:



The procedure of Example 1 is followed, where the comonomer is 4'-acetoxy-2,5-dichlorobenzophenone (0.20 g; 0.65 mmol). Approximately 5% of the sidechain appendages of the resulting rigid-rod copolymer contain reactive ester groups. Even greater reactivity may be imparted by hydrolyzing the ester groups to phenolic groups (e.g. by refluxing in 10% HCl in ethanol for six to twelve hours and then neutralizing with sodium hydroxide).

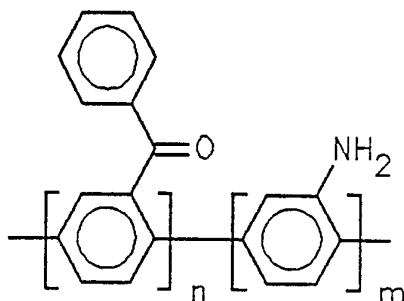
4'-Acetoxy-2,5-dichlorobenzophenone is prepared by treating 4'-Hydroxy-2,5-dichlorobenzophenone, which is prepared by the Friedel-Crafts acylation of phenol with 2,5-dichlorobenzoyl-chloride, with acetyl chloride.

1

EXAMPLE 3.**Preparation of a macromonomer of the structure:**

5

10



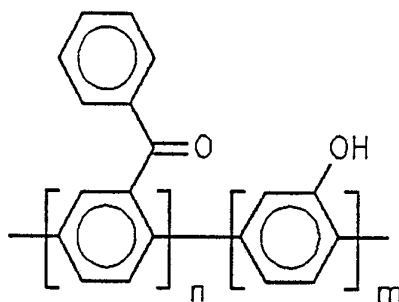
The procedure of Example 1 is followed where the comonomer is 2,5-dichlorophenylsuccinimide (0.17 g; 0.70 mmol). The isolated material is refluxed in 10% HCL in ethanol for six hours and then neutralized with sodium hydroxide. Approximately 5% of the sidechain appendages of the resulting rigid-rod copolymer contain reactive amine groups.

20

EXAMPLE 4.**Preparation of a macromonomer of the structure:**

25

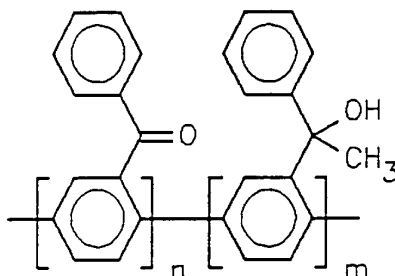
30



The procedure of Example 1 is followed, where the comonomer is the tetrahydropyranyl ether of 2,5-dichlorophenol (0.17 g; 0.69 mmol). The isolated material is refluxed in 10% HCL in ethanol for six hours and then neutralized with sodium hydroxide. Approximately 5% of the sidechain appendages of the resulting rigid-rod copolymer contain reactive hydroxy groups.

EXAMPLE 5.

Preparation of a macromonomer of the structure:



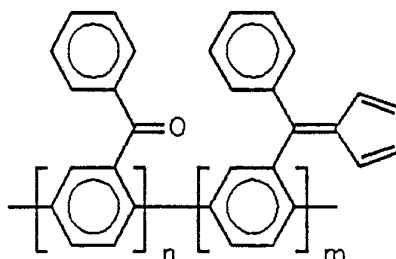
A solution of parapolybenzoylphenylene (0.5 g; 2.8 mmol of monomer units) in 50 ml of diphenyl ether is treated with 0.2 ml (0.28 mmol) of 1.4 molar methyl lithium (ether solution) and heated at 100°C for 2-3 days. This mixture is poured into 1 molar sulfuric acid in ethanol to hydrolyze the lithio salt and precipitate the product. Approximately 10% of the sidechain appendages of the resulting rigid-rod copolymer contain reactive hydroxy groups.

Parapolybenzoylphenylene is prepared as follows: Anhydrous bis(triphenylphosphine) nickel(II) chloride (0.25 g; 0.39 mmol), triphenylphosphine (0.60 g; 2.29 mmol), sodium iodide (0.175 g; 1.17 mmol), and 325 mesh activated zinc powder (1.3 g; 20 mmol) are placed into a flask under an inert atmosphere along with 7 ml of anhydrous N-methylpyrrolidinone (NMP). This mixture is stirred for about 10 minutes at room temperature, leading to a deep-red coloration. A solution of 2,5-dichlorobenzophenone monomer (4.0 g; 16 mmol) in 8 ml of anhydrous NMP is then added by syringe. After stirring for about 12 hours at 50-60°C, the resulting viscous solution is poured into 100 ml of 1 molar hydrochloric acid in ethanol to dissolve the excess zinc metal and to precipitate the polymer. This suspension is filtered and the precipitate triturated with acetone and dried to afford a light yellow to white powder.

1

EXAMPLE 6.**Preparation of a macromonomer of the structure:**

5



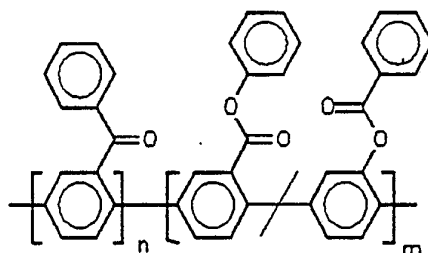
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A solution of parapolybenzoylphenylene (1.0 g; 5.6 mmol of monomer units) in 100 ml of diphenyl ether is treated with 0.25 ml (0.5 mmol) of 2 molar sodium cyclopentadienide (tetrahydrofuran solution) and heated at 100°C for 4 hours. This mixture is poured into 1 molar hydrochloric acid in ethanol to precipitate the product. Approximately 9% of the sidechain appendages of the resulting rigid-rod copolymer contain reactive fulvene groups.

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EXAMPLE 7.**Preparation of a macromonomer of the structure:**

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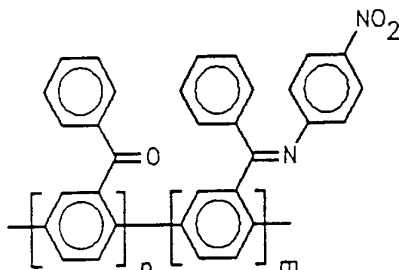
A solution of parapolybenzoylphenylene (0.5 g; 2.8 mmol of monomer units) in 50 ml of methylene chloride is treated with 0.1 g (0.29 mmol) of 50% 3-chloroperoxybenzoic acid (MCPBA) and refluxed for 7 days. This mixture is poured into acetone to precipitate the product. Approximately 10% of the sidechain appendages of the resulting rigid-rod copolymer contain reactive ester groups.

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-48-

EXAMPLE 8.

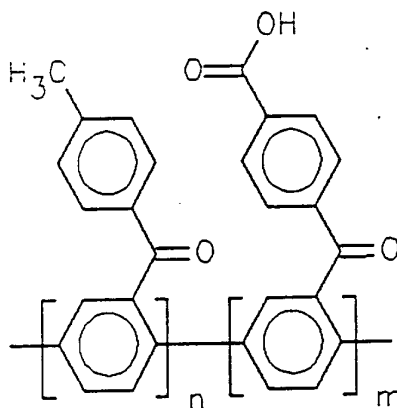
Preparation of a macromonomer of the structure:



A solution of parapolybenzoylphenylene (0.5 g; 2.8 mmol of monomer units) and 4-nitroaniline (25 mg; 0.18 mmol) in 50 ml of NMP is refluxed for 48 hours. This mixture is poured into ethanol to precipitate the product. Approximately 6.5% of the sidechain appendages of the resulting rigid-rod copolymer contain reactive nitro groups.

EXAMPLE 9.

Preparation of a macromonomer of the structure:



A mixture of parapolytoluoylphenylene (0.5 g; 2.6 mmol of monomer units) and potassium permanganate (0.16 g; 1.0 mmol) in 50 ml of glacial acetic acid is refluxed for 18 hours. This mixture is poured into ethanol, and the product removed by filtration. Approximately 10-20% of the sidechain appendages of the

1 resulting rigid-rod copolymer contain reactive carboxy groups.

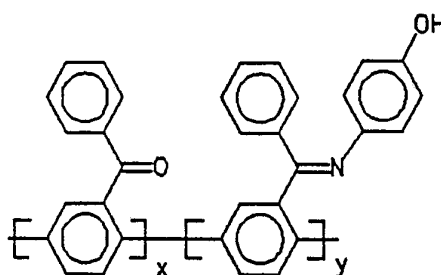
Parapolytoluoylphenylene is prepared in the same manner as parapolybenzoylphenylene, except that a solution of 2,5-dichloro-4'-methylbenzophenone monomer in anhydrous NMP is used in place of 2,5-dichlorobenzophenone.

EXAMPLE 10.

Preparation of a macromonomer of the structure:

10

15



A solution of parapolybenzoylphenylene (500 g; 2.78 mol of monomer units), 4-aminophenol (30 g; 0.278 mol), and p-toluenesulfonic acid monohydrate (1.9 g; 0.01 mol) in chlorobenzene (5 l) is heated to 80°C for 48 hrs. This mixture is poured into ethanol to precipitate the product. Approximately 10% of the sidechain appendages of the resulting rigid-rod copolymer contain reactive phenol groups.

25

EXAMPLE 11.

Preparation of a nylon-6/polyparaphenylene graft copolymer.

30 The procedure of Kohan for the preparation of poly-ε-caprolactam (Nylon-6) given in *Macromolecular Synthesis*, J.A. Moore, Ed., John Wiley & Sons; New York (1977), Coll. Vol. 1, pp. 91-94 (incorporated herein by this reference), is followed, except that 2.5 g of the ester-functionalized macromonomer of Example 1 is added along with the ε-caprolactam. More specifically, a 38 x 300 mm Pyrex® test tube fitted with 8 mm Pyrex® inlet and exit tubes is

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1 charged with ϵ -caprolactam (50 g), the ester-
functionalized macromonomer of Example 1 (2.5 g), and a
50% by weight aqueous solution of an amine salt as
catalyst. The tube is swept with nitrogen for 5 minutes,
5 after which the nitrogen flow rate is adjusted to 350 cc.
per minute. The tube is immersed to a depth of 9 inches
in a 280-285° vapor bath. After 4 hours, the test tube
is removed from the bath and allowed to cool to room
temperature. A polymer plug, which can be cut to a
10 desired particle size, is obtained by breaking the test
tube away from the polymer. The polymer can then be
extracted. The resulting resin is approximately 5% by
weight rigid-rod.

A 50% by weight aqueous solution of an amine salt
15 catalyst is prepared by dissolving or dispersing in water
an amine, such as hexamethylenediamine, piperazine,
3,3'-(methyylimino)bispropylamine, 3,3'-iminobispropylamine,
m-xylylene diamine, and the like; dissolving or dispersing
in water an acid, such as adipic acid, sebacic acid, and
20 the like; and then slowly adding one solution to the
other. Impurities can be removed by treating the
resulting solution with Darco G-60, and the filtrate can
be used directly as the catalyst. Stoichiometric
equivalents of the amine and acid are used, unless the
25 amine is somewhat volatile, in which case a 1% excess of
the amine is used. Amino acids are also suitable for
preparation of an amine salt catalyst.

EXAMPLE 12.

30 Preparation of an aromatic polyester-derived graft
copolymer.

In a flamed 500 ml flask equipped with a magnetic
stirrer, 9.931 g (43.50 mmol) of bisphenol-A, 8.894 g
(43.81 mmol) of isophthaloyl dichloride, 2.362 g (0.62
35 mmol of phenolic groups) of the phenolic functionalized
macromonomer of Example 1, and 15 ml of pyridine in 100
ml of tetrachloroethane are added under nitrogen pressure

-51-

1 and heated at 120°C for 20 hours. The copolymer is
precipitated in methanol, filtered, redissolved in
chloroform, reprecipitated in methanol, filtered, and
dried at 80-100°C in vacuo. The resulting graft copolymer
5 is approximately 13% by weight rigid-rod.

EXAMPLE 13.

**Preparation of an epoxy resin containing a rigid-rod
macromonomer.**

10 The macromonomer of Example 9 (10 g) is mixed with
the diglycidyl ether of bisphenol-A (150 g) (EPON 825,
commercially available from Shell Chemical Co.) with
warming. After the macromonomer has dissolved to the
fullest extent possible, triethylene tetramine (10 g) is
15 added to initiate curing. The resin is applied immediately
after adding the curing agent, and is fully cured in 24
hours.

EXAMPLE 14.

20 **A macromonomer additive for polyamide modification.**

The macromonomer of Example 1 (500 g) is blended with
polyhexamethylene adipamide (5 kg) in a laboratory scale
extruder to form a concentrate. The concentrate is tumble
blended with polyhexamethylene adipamide pellets in a 1
25 to 5 ratio. The mixed pellets are used to fabricate parts
via injection molding. The resulting molded objects have
approximately 2% rigid-rod macromonomer incorporated by
at least partial transamidation-transesterification which
occurs during blending and molding.

30

EXAMPLE 15.

Rigid-Rod Macromonomer-reinforced polystyrene.

The macromonomer of Example 6 (12 g) is mixed with
styrene (150 g) (freed of inhibitor by distillation under
35 reduced pressure) and benzoyl peroxide (3g) in an
evacuatable mold. The mold is degassed and sealed under

-52-

1 vacuum. The mold is held at 55-60°C for 3 days. The mold
is cooled, and opened to release the finished part.

EXAMPLE 16.

5 **Rigid-Rod Macromonomer-reinforced fiberglass.**

The macromonomer of Example 6 (100 g) is blended with
a general purpose unsaturated polyester resin (5 kg) and
methylethylketone peroxide (50 g) catalyst and the
resulting mixture is applied to glass fiber matting in a
10 mold, using standard hand lay-up techniques. Peak curing
temperature is about 110°-130°C, and curing time is about
30 min.

The above descriptions of exemplary embodiments of
15 macromonomers having functional side groups, the rigid-rod
polymers, copolymers, and resins prepared therefrom, and
the processes for making same are illustrative of the
present invention. Because of the variations which will
be apparent to those skilled in the art, however, the
20 present invention is not intended to be limited to the
particular embodiments described above. The scope of the
invention is defined in the following claims.

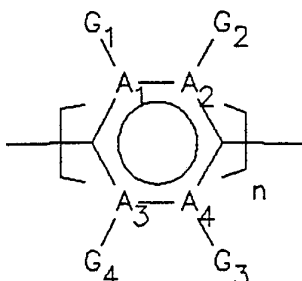
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1 WHAT IS CLAIMED IS:

1. A rigid-rod macromonomer of the formula:



wherein each A_1 , A_2 , A_3 , and A_4 , on each monomer unit, independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each monomer unit, independently, is selected from the group consisting of H, solubilizing side groups, reactive side groups, and reactive solubilizing side groups, provided that at least one monomer unit has at least one reactive side group or reactive solubilizing side group selected from the group consisting of acetals, acetals from ethylvinylether, acetylenes, acid anhydrides, acrylamides, acrylates, alkanols, alkyl aldehydes, alkyl halides, alkyl nitriles, aryl aldehydes, anilines, azides, benzocyclobutenes, biphenylenes, carbonates, carboxylic acids and their salts, carboxylic acid halides, cyanates, epoxides, fulvenes, halides, heteroaryls, hydrazines, hydroxylamines, imides, imines, isocyanates, ketals, maleimides, nadimides, olefins, phenols, phosphates, phosphonates, quaternary amines, silanes, silicates, silicones, sulfonic acids and their salts, sulfonyl halides, tetrahydropyranyl ethers, thioethers, urethanes, vinyl ethers, and vinyls; and provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer has a degree of polymerization, DP_n , greater than about 6; and adjacent monomer units are oriented head-to-head, head-to-tail, or randomly.

1 2. A macromonomer according to claim 1, wherein at
least one monomer unit has at least one reactive side
group selected from the group consisting of aniline,
substituted anilines and chemically protected forms of
5 aniline and substituted aniline.

 3. A macromonomer according to claim 1, wherein
at least one monomer unit has an aminobenzoyl reactive
side group.

10 4. A macromonomer according to claim 1, wherein
at least one monomer unit has an aminophenoxyphenyl
reactive side group.

15 5. A macromonomer according to claim 1, wherein
at least one monomer unit has at least one reactive side
group selected from the group consisting of phenol,
substituted phenols and chemically protected forms of
phenol and substituted phenols.

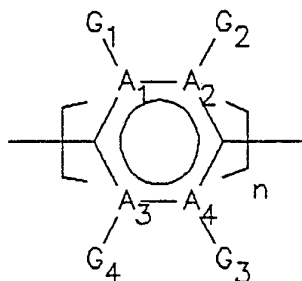
20 6. A macromonomer according to claim 1, wherein
at least one monomer unit has a hydroxyalkyl reactive side
group.

25 7. A macromonomer according to claim 1, wherein
at least one monomer unit has a maleimide reactive side
group.

 8. A macromonomer according to claim 1, wherein
30 at least one monomer unit has a nadimide reactive side
group.

 9. A macromonomer according to claim 1, wherein
the solubilizing side groups are selected from the group
35 consisting of alkyls, amides, aryls, aryl ketones, aryl
sulfides, aryl sulfones, esters, ethers, thioethers,
ketones, and fluorine-substituted analogs of same.

10. A method of making a macromonomer of the formula:



where each A_1 , A_2 , A_3 , and A_4 , on each monomer unit, independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each monomer unit, independently is selected from the group consisting of H, solubilizing side groups, reactive side groups, and reactive solubilizing side groups, provided that at least one monomer unit has at least one reactive side group or reactive solubilizing side group selected from the group consisting of acetals, acetals from ethylvinylether, acetylenes, acid anhydrides, acrylamides, acrylates, alkanols, alkyl aldehydes, alkyl halides, alkyl nitriles, aryl aldehydes, anilines, azides, benzocyclobutenes, biphenylenes, carbonates, carboxylic acids and their salts, carboxylic acid halides, cyanates, epoxides, fulvenes, halides, heteroaryls, hydrazines, hydroxylamines, imides, imines, isocyanates, ketals, maleimides, nadimides, olefins, phenols, phosphates, phosphonates, quaternary amines, silanes, silicates, silicones, sulfonic acids and their salts, sulfonyl halides, tetrahydropyranyl ethers, thioethers, urethanes, vinyl ethers, vinyls; and provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the corresponding G_1 , G_2 , G_3 or G_4 is nil; the macromonomer has a degree of polymerization, DP_n , greater than about 6; and adjacent monomer units are oriented head-to-head, head-to-tail, or randomly,

1 comprising: reductive coupling of substituted
1,4-dihaloaromatic compounds.

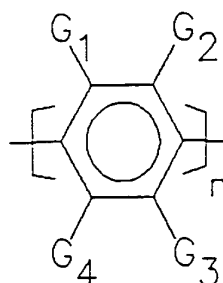
11. A method according to claim 10, wherein the
5 reductive coupling is catalyzed by nickel salts using a
reducing agent selected from the group consisting of zinc,
manganese, and magnesium.

12. A method according to claim 10 wherein the
10 coupling is catalyzed by nickel salts in the presence of
a phosphine ligand, using zinc as a reducing agent.

13. A method according to claim 10, wherein the
1,4-dihaloaryl compounds are treated with magnesium to
15 form Grignard reagents, which are then coupled using a
nickel compound as a catalyst.

14. A rigid-rod macromonomer of the formula:

20



25

wherein each G_1 , G_2 , G_3 , and G_4 , on each monomer unit,
30 independently, is selected from the group consisting of
H, solubilizing side groups, reactive side groups, and
reactive solubilizing side groups, provided that at least
one monomer unit has at least one reactive side group or
reactive solubilizing side group selected from the group
35 consisting of acetals, acetals from ethylvinylether,
acetylenes, acid anhydrides, acrylamides, acrylates,
alkanols, alkyl aldehydes, alkyl halides, aryl aldehydes,

1 anilines, azides, benzocyclobutenes, biphenylenes,
carbonates, carboxylic acids and their salts, carboxylic
acid halides, cyanates, epoxides, formyls, fulvenes,
halides, heteroaryls, hydrazines, hydroxylamines, imides,
5 imines, isocyanates, ketals, maleimides, nadimides,
nitriles, olefins, phenols, phosphates, phosphonates,
quaternary amines, silanes, silicates, silicones, sulfonic
acids and their salts, sulfones, sulfonyl halides,
sulfoxides, tetrahydropyranyl ethers, thioethers,
10 urethanes, vinyl ethers, and vinyls; the macromonomer has
a degree of polymerization, DP_n , greater than about 6; and
adjacent monomer units are oriented head-to-head,
head-to-tail, or randomly.

15 15. A macromonomer according to claim 14, wherein
the solubilizing side groups are selected from the group
consisting of alkyls, amides, aryls, aryl ketones, aryl
sulfides, aryl sulfones, esters, ethers, thioethers,
ketones, and fluorine-substituted analogs of thereof.

20 16. A macromonomer according to claim 14, wherein
at least one monomer unit has an arylketone solubilizing
side group, and at least one monomer unit has an amine-
derived reactive side group.

25 17. A macromonomer according to claim 14, wherein
at least one monomer unit has an arylketone solubilizing
side group, and at least one monomer unit has a reactive
side group selected from the group consisting of amides,
30 carboxylic acids, carboxylic acid halides, carboxylic
anhydrides, and esters.

35 18. A macromonomer according to claim 14, wherein
at least one monomer unit has an arylketone solubilizing
side group, and at least one monomer unit has a reactive
side group comprising an alcohol.

1 19. A macromonomer according to claim 14, wherein
at least one monomer unit has an arylketone solubilizing
side group, and at least one monomer unit has a reactive
side group selected from the group consisting of epoxide,
5 vinyl, and imide groups.

 20. A macromonomer according to claim 14, wherein
at least one monomer unit has an aryl solubilizing side
group, and at least one monomer unit has an amine-derived
10 reactive side group.

 21. A macromonomer according to claim 14, wherein
at least one monomer unit has an aryl solubilizing side
group, and at least one monomer unit has a reactive side
15 group selected from the group consisting of amides,
carboxylic acids, carboxylic acid halides, carboxylic
anhydrides, and esters.

 22. A macromonomer according to claim 14, wherein
20 at least one monomer unit has an aryl solubilizing side
group, and at least one monomer unit has a reactive side
group comprising an alcohol.

 23. A macromonomer according to claim 14, wherein
25 at least one monomer unit has an aryl solubilizing side
group, and at least one monomer unit has a reactive side
group selected from the group consisting of epoxide,
vinyl, and imide groups.

 24. A macromonomer according to claim 14, wherein
30 at least one monomer unit has an aryl ether solubilizing
side group, and at least one monomer unit has an amine-
derived reactive end group.

 25. A macromonomer according to claim 14, wherein
35 at least one monomer unit has an aryl ether solubilizing
side group, and at least one monomer unit has a reactive

1 side group selected from the group consisting of amides,
carboxylic acids, carboxylic acid halides, carboxylic
anhydrides, and esters.

5 26. A macromonomer according to claim 14, wherein
at least one monomer unit has an aryl ether solubilizing
side group, and at least one monomer unit has a reactive
side group comprising an alcohol.

10 27. A macromonomer according to claim 14, wherein
at least one monomer unit has an aryl ether solubilizing
side group, and at least one monomer unit has a reactive
side group selected from the group consisting of epoxide,
vinyl, and imide groups.

15 28. A macromonomer according to claim 14, wherein
at least one monomer unit has an amide solubilizing side
group, and at least one monomer unit has an amine-derived
reactive side group.

20 29. A macromonomer according to claim 14, wherein
at least one monomer unit has an amide solubilizing side
group, and at least one monomer unit has a reactive side
group selected from the group consisting of amides,
25 carboxylic acids, carboxylic acid halides, carboxylic
anhydrides, and esters.

30 30. A macromonomer according to claim 14, wherein
at least one monomer unit has an amide solubilizing side
group, and at least one monomer unit has a reactive side
group comprising an alcohol.

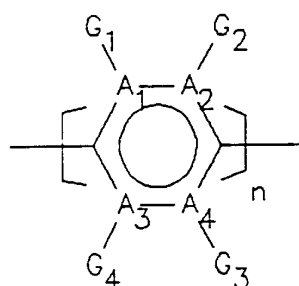
1 31. A macromonomer according to claim 14, wherein
 at least one monomer unit has an amide solubilizing side
 group, and at least one monomer unit has a reactive side
 group selected from the group consisting of epoxide,
 5 vinyl, and imide groups.

32. A. macromonomer according to claim 14, wherein
 a first predetermined number of monomer units have at
 least one solubilizing side group comprising a benzoyl
 10 group, and a second predetermined number of monomer units
 have at least one reactive side group comprising a
 carbomethoxy group.

33. A macromonomer according to claim 14, wherein
 15 a first predetermined number of monomer units have at
 least one solubilizing side group comprising a benzoyl
 group, and a second predetermined number of monomer units
 have at least one reactive side group comprising a
 benzylhydroxy group.

20 34. A method of making a macromonomer having the
 structure

25



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wherein each A₁, A₂, A₃ and A₄, on each monomer unit,
 independently, is C or N; each G₁, G₂, G₃, and G₄, on each
 35 monomer unit, independently, is selected from the group
 consisting of H, solubilizing side groups, reactive side
 groups, and reactive solubilizing side groups, provided

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1 that at least one monomer unit has at least one reactive
side group or reactive solubilizing side group, and
provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
5 has a degree of polymerization, DP_n , greater than about
6; and adjacent monomer units are oriented head-to-head,
head-to-tail, or randomly, comprising:

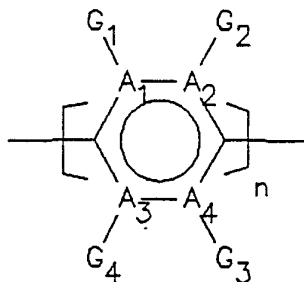
preparing a homopolymer having a rigid-rod backbone;
and

10 reacting said homopolymer with a sufficient
amount of a reagent to yield a macromonomer as described
above.

35. A method according to claim 34, wherein the
15 homopolymer is prepared by reductive coupling of
substituted 1,4-dihaloaromatic monomers.

36. A method of making a macromonomer having the
structure

20



25

30 wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each
monomer unit, independently, is selected from the group
consisting of H, solubilizing side groups, reactive side
groups, and reactive solubilizing side groups, provided
35 that at least one monomer unit has at least one reactive
side group or reactive solubilizing side group, and
provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the

1 corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer has a degree of polymerization, DP_n , greater than about 6; and adjacent monomer units are oriented head-to-head, head-to-tail, or randomly, comprising:

5 preparing a homopolymer having a rigid-rod backbone and pendant, solubilizing side groups; and

reacting said homopolymer with a sufficient amount of a reagent to convert a predetermined number of the solubilizing side groups into reactive side groups.

10

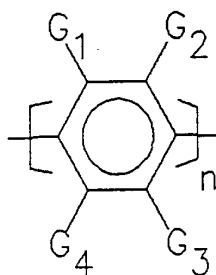
37. A method according to claim 36, wherein the homopolymer is parapoly-4-phenoxybenzoylphenylene.

15 38. A method according to claim 36, wherein the homopolymer is a parapolybenzoylphenylene.

39. A method according to claim 36, wherein the homopolymer is a parapolytoluoylphenylene.

20 40. A method of making a macromonomer of the formula:

25



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35 where each G_1 , G_2 , G_3 , and G_4 , on each monomer unit, independently, is selected from the group consisting of H, solubilizing side groups, reactive side groups, and

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1 reactive solubilizing side groups, provided that at least
 one monomer unit has at least one reactive side group or
 reactive solubilizing side group selected from the group
 consisting of acetals, acetals from ethylvinylether,
 5 acetylenes, acid anhydrides, acrylamides, acrylates,
 alkanols, alkyl aldehydes, alkyl halides, alkyl nitriles,
 aryl aldehydes, anilines, azides, benzocyclobutenes,
 biphenylenes, carbonates, carboxylic acids and their
 salts, carboxylic acid halides, cyanates, epoxides,
 10 fulvenes, halides, heteroaryls, hydrazines,
 hydroxylamines, imides, imines, isocyanates, ketals,
 maleimides, nadimides, olefins, phenols, phosphates,
 phosphonates, quaternary amines, silanes, silicates,
 silicones, sulfonic acids and their salts, sulfonyl
 15 halides, tetrahydropyranyl ethers, thioethers, urethanes,
 vinyl ethers, and vinyls; the macromonomer has a degree
 of polymerization, DP_n , greater than about 6; and adjacent
 monomer units are oriented head-to-head, head-to-tail or
 randomly, comprising: catalytic coupling of substituted
 20 4-halobenzeneboronic acid in the presence of substituted
 dihalobenzenes or substituted benzeneboronic acids.

41. A method of producing reinforced polymers,
 comprising copolymerizing macromonomers having the
 25 structure:



wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
 independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each

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1 monomer unit, independently, is selected from the group
consisting of H, solubilizing side groups, reactive side
groups, and reactive solubilizing side groups, provided
5 side group or reactive solubilizing side group, and
provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
has a degree of polymerization, DP_n , greater than about
10 head-to-tail, or randomly; with one or more monomers.

42. A method according to claim 41, wherein said one
or more monomers are condensation monomers.

15 43. A method according to claim 42, wherein the
polymerization occurs during Reaction Injection Molding

44. A method according to claim 43, wherein the
monomer is caprolactam.

20

45. A method according to claim 41, wherein said
one or more monomers are addition monomers.

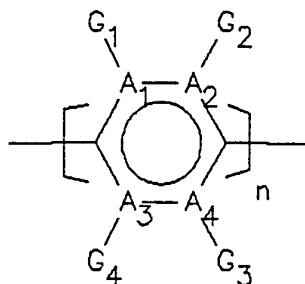
25 46. A method according to claim 45, wherein said
addition monomers are selected from the group consisting
of alkylmethacrylates, butadiene, dicyclopentadiene,
ethylene, propylene, styrene, tetrafluoroethylene, vinyl
acetate, and vinyl chloride.

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1 47. A method of producing reinforced polymers,
 comprising physically blending macromonomers having the
 structure:



wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
 15 independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each
 monomer unit, independently, is selected from the group
 consisting of H, solubilizing side groups, reactive side
 groups, and reactive solubilizing side groups, provided
 that at least one monomer unit has at least one reactive
 20 side group or reactive solubilizing side group, and
 provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
 corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
 has a degree of polymerization, DP_n , greater than about 6;
 and adjacent monomer units are oriented head-to-head,
 25 head-to-tail, or randomly, with one or more preformed
 polymers.

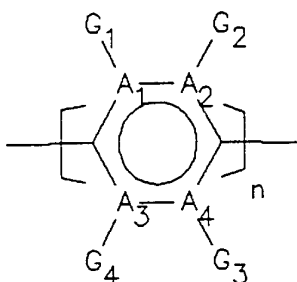
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1 48. A method of producing reinforced polymers
comprising:

 mixing macromonomers having the structure



 wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
15 independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each
monomer unit, independently, is selected from the group
consisting of H, solubilizing side groups, reactive side
groups, and reactive solubilizing side groups, provided
20 that at least one monomer unit has at least one reactive
side group or reactive solubilizing side group, and
provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
has a degree of polymerization, DP_n , greater than about
6; and adjacent monomer units are oriented head-to-head,
25 head-to-tail, or randomly, with one or more preformed
polymers; and

 forming chemical bonds between the macromonomers
and said one or more preformed polymers, wherein bond
formation proceeds in an order selected from the group
30 consisting of bond formation simultaneous with mixing,
bond formation subsequent to mixing, and bond formation
both simultaneous with and subsequent to mixing of the
macromonomers and said one or more preformed polymers.

35 49. A method according to claim 48, wherein the
mixing process comprises melt blending.

1 50. A method according to claim 48, wherein the
mixing process comprises solution blending.

5 51. A method according to claim 48, wherein the
chemical bonds are formed during injection molding.

 52. A method according to claim 48, wherein said one
or more preformed polymers is selected from the group
consisting of polyamides, polyimides, polyesters,
10 polycarbonates, polyphenylene oxide, polyphenylene
sulfide, polyamide-imides, polyamide-esters, polyamide-
ethers, polycarbonate-esters, polyamide-ethers,
polystyrene, polyethylene, polypropylene,
polyvinylchloride, polyacrylates, polyvinylalcohol,
15 polyvinylacetate, polybutadiene, polydicyclopentadiene,
and copolymers thereof.

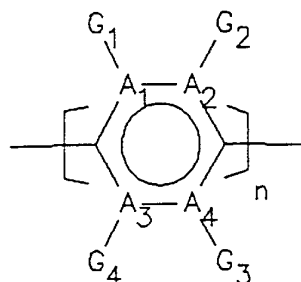
 53. A method according to claim 48, wherein said one
or more preformed polymers is a polyamide and the
20 macromonomers have reactive side groups selected from the
group consisting of carboxylic acids, amides, esters,
amines, anilines, hydroxyls, and phenols.

 54. A method according to claim 48, wherein said one
25 or more preformed polymers is a polyester and the
macromonomers have reactive side groups selected from the
group consisting of carboxylic acids, amides, esters,
amines, anilines, hydroxyls, and phenols.

30 55. A method according to claim 48, wherein said one
or more preformed polymers is a polycarbonate and the
macromonomers have reactive side groups selected from the
group consisting of carboxylic acids, amides, esters,
amines, anilines, hydroxyls, and phenols.

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1 56. A method of producing thermoset epoxide
polymers, comprising reacting a macromonomer having the
structure:

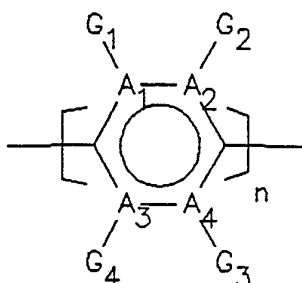


15 wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each
monomer unit, independently, is selected from the group
consisting of H, solubilizing side groups, reactive side
groups, and reactive solubilizing side groups, provided
20 that at least one monomer unit has at least one reactive
side group or reactive solubilizing side group, and
provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
has a degree of polymerization, DP_n , greater than about
6; and adjacent monomer units are oriented head-to-head,
25 head-to-tail, or randomly, with a diepoxide or polyepoxide
to form a crosslinked resin containing rigid segments
derived from said macromonomer.

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1 57. A method of producing thermoset phenolic
 polymers, comprising reacting a macromonomer having the
 structure:



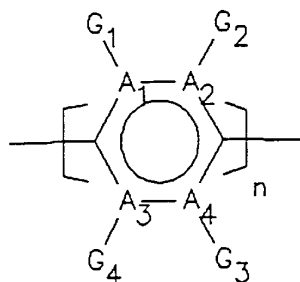
15 wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
 independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each
 monomer unit, independently, is selected from the group
 consisting of H, solubilizing side groups, reactive side
 groups, and reactive solubilizing side groups, provided
 that at least one monomer unit has at least one
 20 phenol-type reactive side group or reactive solubilizing
 side group, and provided that when any of A_1 , A_2 , A_3 , and
 A_4 is N, the corresponding G_1 , G_2 , G_3 , or G_4 is nil; the
 macromonomer has a degree of polymerization, DP_n , greater
 than about 6; and adjacent monomer units are oriented
 25 head-to-head, head-to-tail, or randomly; with one or more
 substances selected from the group consisting of
 formaldehyde, paraformaldehyde, trioxane, phenol-formalde-
 hyde resins, novalac resins, resole resins, and
 resorcinol-formaldehyde resins.

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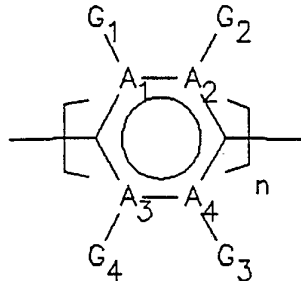
58. A method of producing thermoset polyimide polymers, comprising reacting a macromonomer having the structure:



wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit, independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each monomer unit, independently, is selected from the group consisting of H, solubilizing side groups, reactive side groups, and reactive solubilizing side groups, provided that at least one monomer unit has at least one amine-type reactive side group or reactive solubilizing side group, and provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer has a degree of polymerization, DP_n , greater than about 6; and adjacent monomer units are oriented head-to-head, head-to-tail, or randomly; with at least one of pyromellitic acid or its anhydride, bisphenoltetracarboxylic acid or its anhydride, benzophenonetetracarboxylic acid or its anhydride, 2,2-bis(3,4-dicarboxyphenyl)-hexa fluoropropane dianhydride (6FDA), biphenyl dianhydride, polyamic acids, and uncured polyamide resins.

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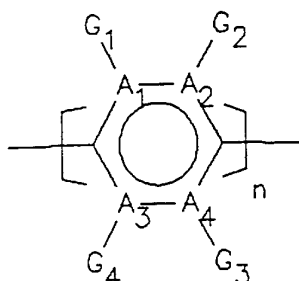
59. A method of producing reinforced thermoset resins, comprising reacting a macromonomer having the structure:



wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit, independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each monomer unit, independently, is selected from the group consisting of H, solubilizing side groups, reactive side groups, and reactive solubilizing side groups, provided that at least one monomer unit has at least one reactive side group or reactive solubilizing side group, and provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer has a degree of polymerization, DP_n , greater than about 6; and adjacent monomer units are oriented head-to-head, head-to-tail, or randomly, with uncured resins selected from the group consisting of allyl resins, bisacetylene resins, bisbenzocyclobutene resins, bisbiphenylene resins, epoxy resins, furan resins, isocyanate resins, maleimide resins, melamine resins, nadimide resins, phenolic resins, silicone resins, unsaturated polyester resins, urea resins, urethanes, and vinyl ester resins.

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1 60. A method of producing a reinforced thermoset resin, comprising reacting a macromonomer having the structure:



15 wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit, independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each monomer unit, independently, is selected from the group consisting of H, solubilizing side groups, reactive side groups, and reactive solubilizing side groups, provided that at least one monomer unit has at least one reactive side group or reactive solubilizing side group, and

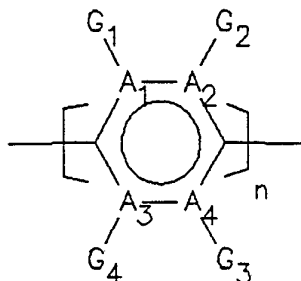
20 provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer has a degree of polymerization, DP_n , greater than about 6; and adjacent monomer units are oriented head-to-head, head-to-tail, or randomly, with a curing agent having

25 reactive groups complementary to said at least one reactive side group or reactive solubilizing side group on the macromonomer and capable of forming covalent crosslinks therewith.

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1 61. A method for producing reinforced polyamides
comprising copolymerization of a macromonomer having the
structure:



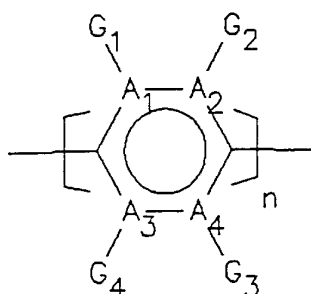
wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
15 independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each
monomer unit, independently, is selected from the group
consisting of H, solubilizing side groups, reactive side
groups, and reactive solubilizing side groups, provided
that at least one monomer unit has at least one reactive
20 side group or reactive solubilizing side group, and
provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
has a degree of polymerization, DP_n , greater than about 6;
and adjacent monomer units are oriented head-to-head,
25 head-to-tail, or randomly, with one or more monomers
capable of producing polyamides.

30

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- 1 62. A polymer comprising:
 a macromonomer having the structure

5



10

 wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
 independently, is C or N; each G_1 , G_2 , G_3 and G_4 , or each
 15 monomer unit, independently, is selected from the group
 consisting of H, solubilizing side groups, reactive side
 groups, and reactive solubilizing side groups, provided
 that at least one monomer unit has at least one reactive
 side group or reactive solubilizing side group, and
 20 provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
 corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
 has a degree of polymerization, DP_n , greater than about 6;
 and adjacent monomer units are oriented head-to-head,
 head-to-tail, or randomly; and

25 at least one monomer having at least one
 reactive group complementary to at least one reactive side
 group or reactive solubilizing side group on the
 macromonomer, polymerized with the macromonomer.

- 30 63. A polymer according to claim 62, wherein said
 at least one reactive side group on the macromonomer is
 selected from the group consisting of acetals, acetals
 from ethylvinylether, acetylenes, acetyls, acid
 anhydrides, acids, acrylamides, acrylates, alcohols,
 35 aldehydes, alkanols, alkyl aldehydes, alkyl halides,
 amides, amines, anilines, aryl aldehydes, azides,
 benzocyclobutenes, biphenylenes, carboxylates, carboxylic

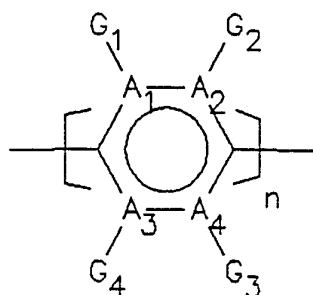
-75-

1 acids and their salts, carboxylic acid halides, carboxylic
 anhydrides, cyanates, cyanides, epoxides, esters, ethers,
 formyls, fulvenes, halides, heteroaryls, hydrazines,
 hydroxylamines, imides, imines, isocyanates, ketals,
 5 ketoalkyls, ketoaryls, ketones, maleimides, nadimides,
 nitriles, olefins, phenols, phosphates, phosphonates,
 quaternary amines, silanes, silicates, silicones, silyl
 ethers, styrenes, sulfonamides, sulfones, sulfonic acids
 and their salts, sulfonyl halides, sulfoxides,
 10 tetrahydropyranyl ethers, urethanes, vinyl ethers,
 thioethers, and vinyls.

64. A polymer comprising:
 a macromonomer having the structure

15

20



25 wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
 independently, is C or N; each G_1 , G_2 , G_3 and G_4 , or each
 monomer unit, independently, is selected from the group
 consisting of H, solubilizing side groups, reactive side
 groups, and reactive solubilizing side groups, provided
 30 that at least one monomer unit has at least one reactive
 side group or reactive solubilizing side group, and
 provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
 corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
 has a degree of polymerization, DP_n , greater than about 6;
 35 and adjacent monomer units are oriented head-to-head,
 head-to-tail, or randomly; and

1 at least one complementary condensation monomer
copolymerized with the macromonomer.

5 65. A polymer according to claim 64, wherein said
at least one condensation monomer is selected from the
group consisting of p-phenylenediamine,
m-phenylenediamine, oxydianiline, methylenedianiline,
terephthalic acid, terephthaloyl chloride, esters of
terephthalic acids, and mixtures thereof.

10 66. A polymer according to claim 65, wherein said
at least one condensation monomer is selected from the
group consisting of hexamethylenediamine, adipic acid,
esters of adipic acid, and adipoyl chloride.

15 67. A polymer according to claim 64, wherein said
at least one complementary condensation monomer is
selected from the group consisting of amino acids,
biscarboxylic acids, biscarboxylic acid chlorides,
20 biscarboxylic acid esters, diamines, diols,
hydroxycarboxylic acids, lactams, and lactones.

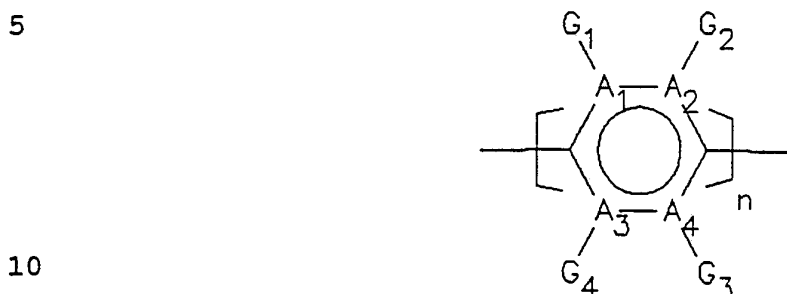
25 68. A polymer according to claim 64, wherein said
at least one complementary condensation monomer comprises
terephthalic acid and ethylene glycol.

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1 69. A reinforced polymeric composition comprising:
 a macromonomer having the structure



wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
15 independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each
monomer unit, independently, is selected from the group
consisting of H, solubilizing side groups, reactive side
groups, and reactive solubilizing side groups, provided
that at least one monomer unit has at least one reactive
20 side group or reactive solubilizing side group, and
provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
has a degree of polymerization, DP_n , greater than about 6;
and adjacent monomer units are oriented head-to-head,
25 head-to-tail, or randomly; and

a flexible polymer covalently attached to the macromonomer.

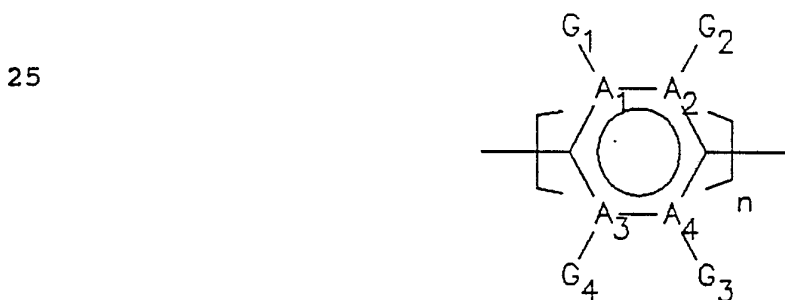
70. A reinforced polymer according to claim 69,
30 wherein the flexible polymer is selected from the group
consisting of polyacetals, polyamides, polyimides,
polyesters, polycarbonates, polyamide-imides, poly-
amide-esters, polyimide-ethers, polycarbonate-esters,
polyamide-ethers, polyalkylmethacrylates, polyethylene,
35 polypropylene, polystyrene, polyvinylacetate, polyvinyl-
chloride, and polyvinylalcohol.

1 with a curing agent having reactive groups
complementary to the reactive side groups, reactive
solubilizing side groups, or both reactive side groups and
reactive solubilizing side groups of the macromonomer and
5 capable of forming covalent crosslinks therewith.

74. A thermoset composition according to claim 73,
wherein said at least one reactive side group or reactive
solubilizing side group is selected from the group
10 consisting of acetylenes, acrylates, alcohols, amine
derived groups, anilines, benzocyclobutenes, biphenylenes,
epoxides, isocyanides, maleimides, nadimides, phenols and
vinyls.

15 75. A thermoset composition according to claim 73,
wherein the curing agent is selected from the group
consisting of diamines, polyamines, diols, polyols,
diepoxides, and polyepoxides.

20 76. A thermoset composition formed by thermally
curing macromonomers having the structure



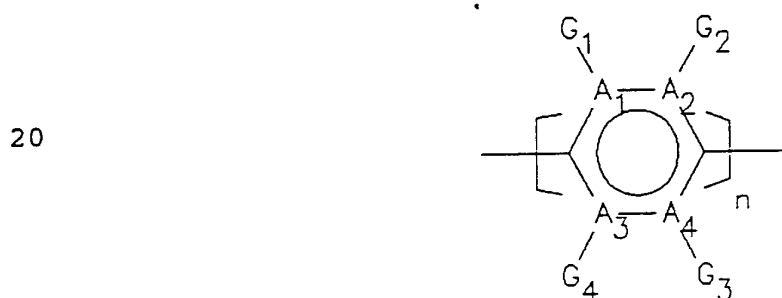
wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
independently, is C or N; each G_1 , G_2 , G_3 and G_4 , or each
monomer unit, independently, is selected from the group
35 consisting of H, solubilizing side groups, reactive side
groups, and reactive solubilizing side groups, provided
that at least one monomer unit of each macromonomer has

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1 at least one reactive side group or reactive solubilizing
 side group, and provided that when any of A_1 , A_2 , A_3 , A_4
 is N, the corresponding G_1 , G_2 , G_3 or G_4 is nil; each
 5 macromonomer has a degree of polymerization, DP_n , greater
 than about 6; and adjacent monomer units are oriented
 head-to-head, head-to-tail, or randomly.

77. A thermoset according to claim 76, wherein said
 at least one reactive side group or reactive solubilizing
 10 side group is selected from the group consisting of
 acetylenes, benzocyclobutenes, biphenylenes, maleimides,
 and nadimides.

78. A reinforced polymeric material comprising:
 15 a macromonomer having the structure



25 wherein each A_1 , A_2 , A_3 , and A_4 , on each monomer unit,
 independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each
 monomer unit, independently, is selected from the group
 consisting of H, solubilizing side groups, reactive side
 30 groups, and reactive solubilizing side groups, provided
 that at least one monomer unit has at least one reactive
 side group or reactive solubilizing side group and
 provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
 corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
 35 has a degree of polymerization, DP_n , greater than about 6;
 and adjacent monomer units are oriented head-to-head,
 head-to-tail, or randomly; and

-81-

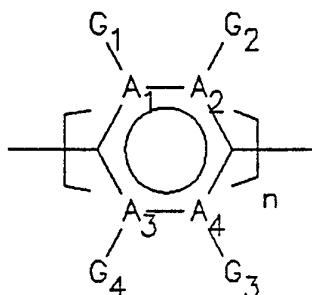
1 at least one addition monomer polymerized with
the macromonomer.

5 79. A reinforced polymeric material according to
claim 78, wherein said at least one addition monomer is
selected from the group consisting of alkylmethacrylates,
butadiene, dicyclopentadiene, ethylene, propylene,
styrene, tetrafluoroethylene, vinyl acetate and vinyl
chloride.

10

80. A reinforced polymer elastomer comprising:
an elastomer having a polymer network; and
rigid segments covalently attached to the
polymer network, derived from macromonomers having the
15 structure

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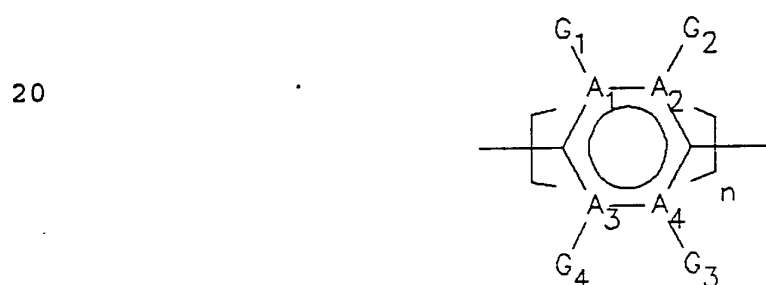
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wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
independently, is C or N; each G_1 , G_2 , G_3 and G_4 , or each
monomer unit, independently, is selected from the group
consisting of H, solubilizing side groups, reactive side
30 groups, and reactive solubilizing side groups, provided
that at least one monomer unit has at least one reactive
side group or reactive solubilizing side group and
provided that when any of A_1 , A_2 , A_3 and A_4 is N, the
corresponding G_1 , G_2 , G_3 or G_4 is nil; the macromonomer has
35 a degree of polymerization, DP_n , greater than about 6;
and adjacent monomer units are oriented head-to-head,
head-to-tail, or randomly.

1 81. A reinforced polymer elastomer according to
 claim 80, wherein the elastomer is selected from the group
 consisting of polybutadiene, copolymers of butadiene with
 one or more other monomers, butadiene-acrylonitrile
 5 rubber, styrene-butadiene rubber, polyisoprene, copolymers
 of isoprene with one or more other monomers,
 polyphosphazenes, natural rubber, and blends of natural
 and synthetic rubber.

10 82. A reinforced polymer elastomer according to
 claim 80, wherein the elastomer is selected from the group
 consisting of polydimethylsiloxane, copolymers containing
 the dimethylsiloxane unit, polydiphenylsiloxane, and
 copolymers containing the diphenylsiloxane unit.

15 83. A reinforced polymeric material, comprising:



wherein each A_1 , A_2 , A_3 and A_4 , on each monomer unit,
 independently, is C or N; each G_1 , G_2 , G_3 , and G_4 , on each
 monomer unit, independently, is selected from the group
 30 consisting of H, solubilizing side groups, reactive side
 groups, and reactive solubilizing side groups, provided
 that at least one monomer unit has at least one reactive
 side group or reactive solubilizing side group, and
 provided that when any of A_1 , A_2 , A_3 , and A_4 is N, the
 35 corresponding G_1 , G_2 , G_3 , or G_4 is nil; the macromonomer
 has a degree of polymerization, DP_n , greater than about

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1 6; and adjacent monomer units are oriented head-to-head,
head-to-tail, or randomly; and
 at least one preformed polymer, blended with the
macromonomer.

5

 84. A reinforced polymeric material according to
claim 83, wherein the preformed polymer is selected from
the group consisting of polyamides, polyimides,
polyesters, polycarbonates, polyamide-imides, poly-
10 amide-esters, polyamide-ethers, polycarbonate-esters, and
polyamide-ethers.

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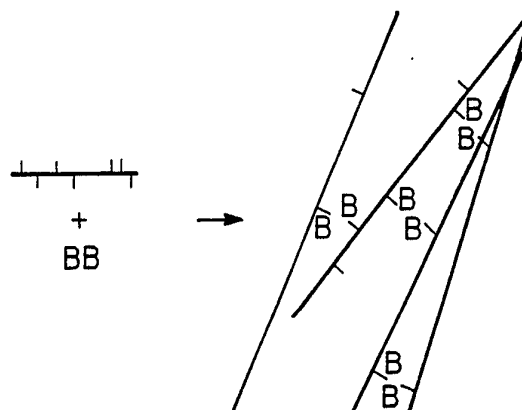
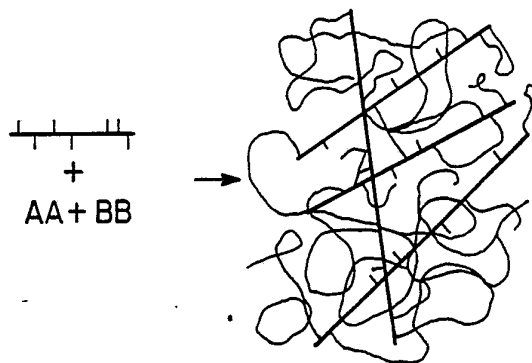
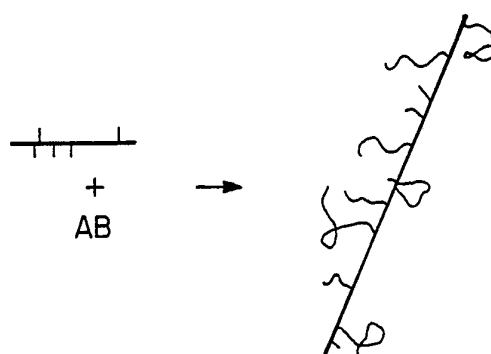
Fig. 1*Fig. 2**Fig. 3*

Fig. 4

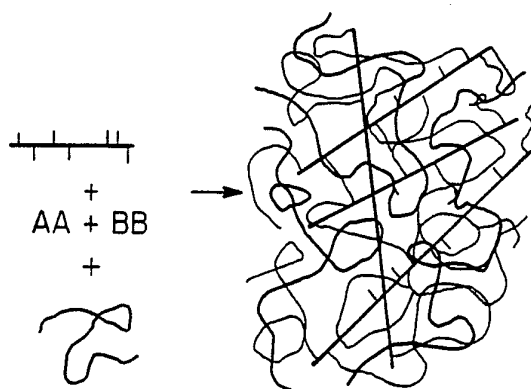


Fig. 5

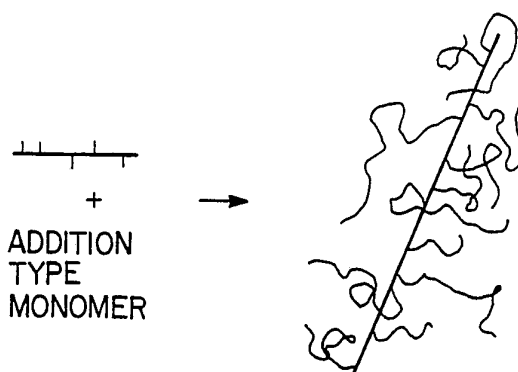
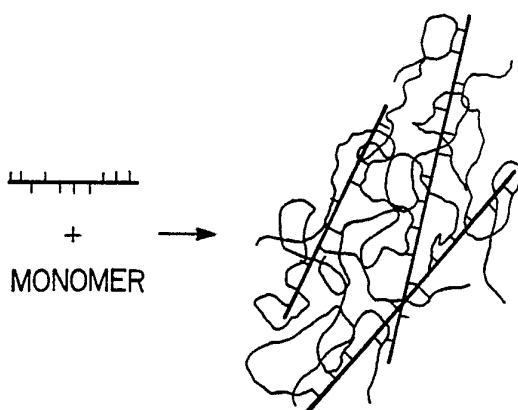


Fig. 6



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/05886**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(5) : C08F 257/00, C08G 61/10, 61/12

US CL : Please See Extra Sheet.

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)

U.S. : 525/242, 276, 290, 298, 416, 418, 471; 528/86, 92, 125, 126, 127, 219, 137, 181, 182, 225, 247, 223, 301, 397, 425, 48, 44, 45, 73

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)

Please See Extra Sheet.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	CA, A, 1,129,418 (COLON et al) 10 August 1982; Page 3, lines 5-24, page 7, lines 8-23.	1, 5, 9 - 15, 17, 21, 25, 29, 32, 40
X	WO, A, WO 91/02764 (MAXDEM INCORPORATED) 07 March 1991; Page 17, line 8 to page 18, line 20.	1-6, 9-32, 40
X	Chemical Abstracts, Vol. 86:139404d (TREVILLYAN) 09 May 1977, entire document.	1-33, 40
X,P	Chemical Abstracts, Vol. 116:21589c (KALLITSIS et al.) 20 January 1992, entire document.	1-33, 40
X	Chemical Abstracts, Vol. 78:98152j (MEZHIKOVSKII et al.) 23 April 1973, entire document.	1-33, 40
X,P	Chemical Abstracts, Vol. 115:280696z (WALLOW et al.) 23 December 1991, entire document.	1-33, 40

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*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
A document defining the general state of the art which is not considered to be part of particular relevance	*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
E earlier document published on or after the international filing date	*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
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	* & * document member of the same patent family
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	

Date of the actual completion of the international search

13 NOVEMBER 1992

Date of mailing of the international search report

11 DEC 1992

Name and mailing address of the ISA/
Commissioner of Patents and Trademarks
Box PCT
Washington, D.C. 20231

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Authorized officer

JEFFREY MULLIS

Telephone No. (703) 308-2351

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US92/05886

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X,P	Chemical Abstracts, Vol. 115:136902w (WALLOW et al.) 30 September 1991, entire document.	1-33,40
X	Chemical Abstracts, Vol. 96:7293p (LIOGON KII et al.) 04 January 1982, entire document.	1-33,40

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

525/242, 276, 290, 298, 416, 418, 471; 528/86, 92, 125, 126, 127, 219, 137, 181, 182, 225, 247, 223, 301, 397, 425, 48, 44, 45, 73

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS: COUPL? (P) (AROMATIC OR PHENYL OR ?PHENYLENE) (P) (NICKEL OR PALLADIUM)

CAS STRUCTURE SEARCH

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

Group I, claims 1-33 and 40-84, drawn to a macromonomer, a process for producing a macromonomer by coupling aromatic dihalides and a process of use thereof, classified in class 525, subclass 242 plus and 528 subclass 86 plus.

Group II, claims 34-39 drawn to a different process for producing a macromonomer by modification of a preformed polymer, classified in class 525, subclass 107 plus.

In addition to the above generic groups, each of Groups I and II contain the following species of "G":

- 1) reactive side groups
- 2) solubilizing side groups
- 3) reactive solubilizing side groups

and it considers that the international application does not comply with the requirements of unity of invention (Rules 13.1, 13.2 and 13.3) for the reasons indicated below:

The three listed groups each perform a different function and as such the three groups do not meet the requirement of a technical interrelationship and the same or corresponding technical features as defined in PCT Rule 13.2.

The group I claims comprise a category of claims drawn to an intermediate and final product, a process of making the intermediate product and a process for use thereof and are properly grouped together as set out in PCT Rule 13.2 as being so linked as to form a single general inventive concept. The invention of Group II is directed to a different process for preparing the intermediate product of Group I and PCT Rule 13.2 does not permit the claiming of multiple processes for preparing the same product.

The lack of unity discussed in the telephone conversation of 20 August 1992 with applicant's attorney, William Christie is superseded by the above lack of unity.