Copolymers and terpolymers comprising randomly repeating units represented by the general formulae

\[
\begin{align*}
\text{OR} \\
\text{OR}
\end{align*}
\]

and

\[
\begin{align*}
\text{OR'} \\
\text{OR}
\end{align*}
\]

wherein the R' radicals contain OH functionality and R being at least one member of the group of monovalent radicals selected from alkyl, substituted alkyl, aryl, substituted aryl and arylalkyl, and R' is represented by

\[
\text{O} - \text{C} - \text{R''}
\]

wherein O represents either \(-(\text{CH}_2)_n\) or \(-\text{C}_n\text{H}_2\text{X}(\text{CH}_2)_m\), the \(-\text{X}(\text{CH}_2)_m\) group being either meta or para and n is an integer from 1 to 6, m is an integer from 1 to 3, X is O or CH₃, and R'' is H or a lower alkyl radical with up to four carbon atoms (methyl, ethyl, etc.). The ratio of R to R' is between 99.5 to 0.5 and 65 to 35.
The polymers of this invention contain small amounts of randomly distributed repeating units in addition to the repeating units described above. The polymers of this invention have a degree of polymerization of 10 to 50,000. Examples of the additional repeating units are:

\[
\begin{align*}
&\text{R} = \text{R'} \\
&\text{R}''
\end{align*}
\]

wherein R and R' are defined as described above and R" represents an organic monovalent radical containing a group with —OH functionality which is capable of further reaction at relatively moderate temperature represented by the formula

\[
\begin{align*}
&\text{OH} \\
&\text{OR, CH}_n
\end{align*}
\]

Optimization of physical and chemical properties of polymers can generally be accomplished by crosslinking reactions. When crosslinked, the polymers of this invention are useful as solvent- and chemical-resistant coatings, sealants, potting compounds, elastomers and plastics. They are particularly suited to applications where flame retardancy is desirable. The polymers of this invention contain hydroxyl sites and can be crosslinked by a variety of chemical agents, including those that contain at least two isocyanate or anhydride sites for subsequent crosslinking; whereas higher molecular weight polymers require much smaller concentrations of R".

In one process for the preparation of the polymers of this invention poly(dichlorophosphazene) is dissolved in a suitable solvent such as benzene, toluene, xylene, chlorobenzene, o-dichlorobenzene, tetrahydrofuran or mixtures thereof. This polymer solution is gradually added to a well stirred solution or suspension of alkoxide salt(s), e.g. as described in U.S. Pat. No. 3,515,688. If preferred, the salt(s) may be added to the solution of poly(dichlorophosphazene). Sodium alkoxides are normally employed but lithium or potassium salts are also suitable. The salts should be present in excess. The total mole percent of salts is preferably in the range 105 to 200 percent based on equivalents of chlorine originally present in the poly(dichlorophosphazene). The alkali salts derived from such alcohols or diols as trifluoroethanol, 2,2,3,3,3-pentafluoropropanol, 2,2,3,3,4,4,4-heptafluorobutanol, 2,2,3,3-tetrafluoropropanol, 2,2,3,3,4,4,5,5,5-pentafluoropentanol, 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptanol, 2,2,3,3,4,4,5,5,5,6,6,7,7,8,8,8-pentafluorooctanol, 1,2-propanediol, 1,3-butanediol, 1,5-hexanediol, 1,2-
The preferred ratio of reactive group of curing agent to hydroxyl group of the polyphosphazene is 1:0.1 to 5% by weight on polyphosphazene and is determined by physical solution techniques. Catalysts may also be present to accelerate the curing reaction. Tertiary amines such as trialkylamines, triethylenediamine N-alkylated derivatives of piperidine, morpholine, and 2,4,6-tris(N,N-dimethylaminomethyl)phenol, metal salts, and metal alkylhalides are representative of suitable catalysts. The amount of catalyst used is generally 0.1 to 5% by weight on polyphosphazene.

The following curing agents are representative of those found suitable for the curing of the polymers of this invention:

A. diisocyanates
1-chloro-2,4-phenylene diisocyanate
p-phenylene diisocyanate
4,4'-diphenylmethane diisocyanate
2,4-toluene diisocyanate
3,3'-dimethyl-4,4'-biphenylene diisocyanate
3,3'-dimethyl-4,4'-diphenylmethane diisocyanate
2,2',5,5'-tetramethyl-4,4'-biphenylene diisocyanate
2,4,6-toluene diisocyanate (80/20)
3,3'-dimethoxy-4,4'-biphenylene diisocyanate
4,4'-biphenylene diisocyanate
3,3'-dichlorobiphenylene diisocyanate
α, α'-xylene diisocyanate
vinylene diisocyanate
polyvinylene polyphenylenediocyanate

B. dianhydrides
pyromellitic dianhydride
3,3', 4,4'-benzophenone tetracarboxylic dianhydride
bis(3,4-dicarboxyphenyl)ether dianhydride
2,2-bis(3,4-biscarboxyphenyl)propane dianhydride
1,2,4,5-cyclohexane tetracarboxylic dianhydride

The above list is for purposes of illustration only and is not intended to be all inclusive. Other polyisocyanates or anhydride crosslinking agents may be used as curing agents.

The amount of curing agent will generally vary from 2 to 50% by weight on polyphosphazene and is determined by the functionality and molecular weight of both the polyphosphazene and the curing agent itself. The preferred ratio of reactive group of curing agent to hydroxyl group of the polyphosphazene is 1.0 to 1.1.

The crosslinking reaction may be performed at ambient or elevated temperatures. For example, a polyphosphazene derived from trifluoroethanol (45 mole percent), 2,2,3,3,4,4,5,5, octafluoropentanol (45 mole percent) and 1,3-butanediol (10 mole percent) when dissolved in tetrahydrofuran can be crosslinked at room temperature in the presence of 2,4-toluene diisocyanate and dibutyltin diacetate catalyst. The same polymer can be crosslinked with dianhydrides but longer times and/or higher temperatures are required.

In these instances, the formulated polymer is applied to the desired substrate or form and subsequently crosslinked in situ upon standing and/or upon application of heat. These crosslinking reactions are often run in the presence of inert, reinforcing or other fillers and the presence of these additives should in no way be construed as falling outside the scope of this invention.

This invention is further illustrated by reference to the following examples which are not intended to limit the scope of the invention.

**EXAMPLE 1**

**Preparation and Cure of a Terpolymer**

An alkoxide mixture was prepared by the reaction of \( \text{CF}_3\text{CH}_2\text{OH} \) (18.0 g, 0.18 mole), \( \text{C}_8\text{F}_8\text{CH}_2\text{OH} \) (36.0 g, 0.18 mole) and \( \text{CH}_3\text{CH(OH)}\text{CH}_2\text{CH(OH)}\text{CH}_3 \) (16.2 g, 0.18 mole) with sodium (10.1 g, 0.44 mole) in 400 ml of dry tetrahydrofuran. The alkoxide mixture was stirred overnight at room temperature and refluxed for 3 hours. The \( \text{C}_8\text{F}_8\text{PN} \) polymer (23.2 g, 0.2 mole) in benzene was added to the alkoxide solution at reflux in about 1.5 hours. After the addition was complete the reaction mixture was stirred for 0.5 hour and allowed to cool to room temperature. The liquid was decanted and the solid portion was washed with water. The solid product was dissolved in 600 ml of the azeotrope of CCl\(_3\)FCCl\(_2\) and acetone and washed with water until the aqueous layer was free of chloride ion. Upon precipitation into benzene, an opaque white rubbery solid (26 g) was obtained. The terpolymer had an intrinsic viscosity of 0.83 dl/g in CCl\(_3\)FCCl\(_2\)/acetone at 28°C. By titration, the CH\(_3\)CH(OH)CH\(_2\)CH\(_2\)OH concentration of the title terpolymer was found to be about 11 mole percent. Anal. Calcd. for the title terpolymer which contains 10 mole percent of CH\(_3\)CH(OH)CH\(_2\)CH\(_2\)O-: C, 22.5; H, 1.6; N, 4.6; Cl, 0.0. Found: C, 22.7; H, 1.7; N, 4.6; Cl, 0.2. The title terpolymer was also prepared with the amount of —OH functionality varying from 0.5 to 35 mole percent by using initial quantities of 0.01 to 0.15 mole, respectively, of \( \text{CH}_3\text{CH(OH)}\text{CH}_2\text{CH(OH)}\text{CH}_3 \) and decreasing the amounts of sodium fluoroalkoxides accordingly.

Separate curing studies with an aliphatic diisocyanate DDI and 2,4-toluene diisocyanate (TDI) were carried out. A 10 percent solution of the above polymer \((\text{I})_{0.83}\) was prepared in the azeotrope of CCl\(_3\)FCCl\(_2\) and acetone, crosslinking agents were added, and the mixture was observed at room temperature. The curing data are summarized in Table 1. In a similar manner the terpolymers of this example were also crosslinked by polyethylene polyphenylenodiocyanate (PAPI, trademark of Upjohn Co.).
The polymer of Example 1 was also cured with 3,3', 4,4'-benzophenone/tetracarboxylic dianhydride by heating at 150°C. The polymer was also cured with 2,4-toluene diisocyanate (TDI) and dibutyltin diacetate catalyst as a coating as follows: a glass sheet was coated with a solution of the polymer and solvent was allowed to evaporate. When the film was slightly tacky, a small amount of a solution of TDI (15% by weight on polymer) and dibutyltin diacetate (0.5% by weight on polymer) was sprayed over it. Further drying led to a crosslinked coating.

**EXAMILES 2-12**

Following the procedure of Example 1, using the indicated amounts of the alcohols and the indicated reaction conditions, the corresponding coand terpolymers of Examples 2-12 were prepared. When reaction temperatures in excess of 70°C were employed, bis(2-methoxyethyl)ether and chlorobenzene were used as solvents for the alkoxides and [Cl,CN], polymer, respectively. The polymers were found to be curable with toluene diisocyanate or the other curing agents listed above.

**EXAMPLE 13**

Alternate Preparation of the Terpolymer of Example 1

A solution of the sodium salt of 1,3-butadienol was added to a solution of 3.43 g [(CF,CH(O)O)zPN-(CF,CH(OH)CH,CF,0-PN]z Terpolymer Cure Mixture 0.005 mole) in 70 ml of (F[C(F,CF)CF,C]CHFCF,)/dioxane (5v/2v). The reaction was stirred overnight at room temperature and then heated 3 hours at 70°C. Polymer was precipitated upon addition of methanol and was isolated as described in Example 1. The product (3.2 g) was a yellowish, weak rubbery solid which had an intrinsic viscosity of 0.80 d/l/g in Freon TA at 28°C. The initial copolymer had an intrinsic viscosity of 0.83 d/l/g. Analysis of product was essentially the same as that described in Example 1. Crosslinking was effected with 2,4-toluene diisocyanate.

Similarly a terpolymer with an intrinsic viscosity of 0.21 d/l/g was prepared. This material was mixed with TDI and dibutyltin diacetate catalyst and poured into an open mold. Upon standing a crosslinked elastomeric mass was produced. This same mixture also served as a sealant material upon crosslinking.

**EXAMPLES 14-17**

Following the procedure of Example 13, but using the homopolymers and copolymers indicated below, the corresponding hydroxyl containing copolymers and terpolymers, respectively, were obtained. All the products could be crosslinked by reaction with 2,4-toluene diisocyanate.
EXAMPLE 18
Preparation of a [(CF₃CH₂O),PN-] Terpolymer

A solution prepared from sodium (0.069 g, 0.003 mole) and 100 ml ethylene glycol was added to a refluxing solution (70°C) of [(CF₂)₃CH₂OH], (1:1 copolymer (11.3 g, 0.03 equiv.) in 300 ml tetrahydrofuran. The reaction was refluxed 4-4.5 hours, cooled and polymer was precipitated. The title terpolymer (6.0 g) was obtained after water washing and drying. A solution of terpolymer in tetrahydrofuran crosslinked upon standing at room temperature in the presence of 2,4-toluene diisocyanate and dibutyltin diacetate catalyst.

EXAMPLES 19-21

Following the procedure of Example 18, using the indicated poly(fluoroalkoxyphosphazene) and glycol, the corresponding curable polymers of examples 19-21 were prepared.

<table>
<thead>
<tr>
<th>Example</th>
<th>Starting Polymer</th>
<th>Polymer Prepared</th>
<th>Glycol Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>19</td>
<td>[(CF₃CH₂O)₃PN]ₙ</td>
<td>[(CF₃CH₂O)₃PN-]</td>
<td>HO(CH₂)₇OH</td>
</tr>
<tr>
<td>20</td>
<td>&quot;</td>
<td>[(CF₃CH₂O)₃PN-]</td>
<td>HO(CH₂)₇OH</td>
</tr>
<tr>
<td>21</td>
<td>(4-CIC₆H₄O)₃PN]</td>
<td>[(CF₃CH₂O)₃PN-]</td>
<td>HO(CH₂)₇OH</td>
</tr>
</tbody>
</table>

We claim:

1. Polyphosphazenes having a degree of polymerization of 10 to 50,000 the skeletal chains of which comprise randomly repeating units represented by the general formulas

\[
\begin{align*}
\text{OR} & \quad \text{N} \\
\text{OR} & \quad \text{N}
\end{align*}
\]

wherein each R is a monovalent radical selected from the group consisting of alkyl, substituted alkyl, fluoroalkyl, aryl, substituted aryl and aryalkyl and not every R in the polyphosphazene is required to be identical to every other R; and each R is a monovalent group containing OH functionality and the ratio of R':R being between 0.5 to 99.5 and 35 to 65.

2. The polymers of claim 1 wherein R is represented by the general formula

\[
\begin{align*}
\text{OR} & \quad \text{N} \\
\text{OR} & \quad \text{N}
\end{align*}
\]

and p are integers from 1 to 8.

3. A terpolymer according to claim 1 in which up to 35 mole percent of the groups attached to the P atoms contain —OH functionality.

4. The polymers of claim 1 as curable compositions which can be crosslinked at room temperature or above.

5. A cured polyphosphazene of claim 1, cured with a polyisocyanate.

6. A cured polyphosphazene of claim 1, cured with a polyanhydride.

7. The polyphosphazenes of claim 1 in which R is CF₃CH₂—.

8. The polyphosphazenes of claim 1 in which R is selected from the group which is comprised of —CH₃(CF₂)mF and —CH₃(CF₂)mH groups where m and p are integers from 1 to 8.
where not every R is required to be identical to every other R with the alkali salt of R, Q, and R'' being as defined in claims 1 and 2.

HOQCHR'' ;

OH

* * * * *