

PATENT SPECIFICATION

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(54) AROMATIC SULFIDE/SULFONE POLYMER PRODUCTION

(71) We, PHILLIPS PETROLEUM COMPANY, a corporation organised and existing under the laws of the State of Delaware, United States of America, of Bartlesville, Oklahoma, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to the production of polymers from aromatic compounds.

In recent years, a wide variety of high polymers have been prepared, many of which are currently being produced and marketed on a large scale. While such polymers are useful in many areas, one property of high polymers, particularly those of the thermoplastic type, which needs to be improved is the ability to withstand high temperature. Since thermoplastic materials can be moulded rapidly and efficiently into almost any desired shape, they lend themselves to mass production. The high polymer, especially a thermoplastic material, which would stand very high temperatures and could be used in such areas as electrical components, wire coatings, automotive parts, and the like has been the objective of a great deal of research.

In accordance with this invention, aromatic sulfide/sulfone polymers exhibiting higher molecular weight than normally obtained are produced by contacting bis-(p-chlorophenyl) sulfone with a hydrated alkali metal sulfide, other than lithium sulfide, under polymerization conditions and in the presence of an organic amide.

Specifically, the polymerization step of the invention is carried out using a hydrated alkali metal sulfide without prior treatment, e.g., a distillation step, to remove the water of hydration, this being found to result in a higher molecular weight product than that obtained when water is removed prior to the polymerization step. This discovery was surprising since previously it had been observed that poly(p-phenylene sulfide) of higher molecular

weight was obtained using p-dichlorobenzene, partially hydrated sodium sulfide, and N-methyl-2-pyrrolidone if the polymerisation step was preceded by distillation of water from a mixture of the partially hydrated sodium sulfide and N-methyl-2-pyrrolidone than if such a distillation step was omitted.

The alkali metal sulfide used in this invention can be sodium sulfide, potassium sulfide, rubidium sulfide, or cesium sulfide, the alkali metal sulfide being at least partially hydrated. If desired, mixtures of alkali metal sulfides can be employed. Optionally, free water as well as water of hydration can be present. Although the sum of the amounts of water present as free water and as water of hydration can vary considerably, generally it will be within the range of from 1 mole to 10 moles, preferably from 2 moles to 9 moles, per mole of alkali metal sulfide. Thus, the alkali metal sulfide composition can comprise a mixture of hydrated alkali metal sulfide and either anhydrous alkali metal sulfide or free water. Examples of some suitable alkali metal sulfides include sodium sulfide nonahydrate, potassium sulfide pentahydrate, rubidium sulfide tetrahydrate, and cesium sulfide tetrahydrate. The alkali metal sulfide presently preferred is sodium sulfide containing about 60 weight percent Na_2S and about 40 weight percent water of hydration, corresponding to an average of about 2.8 molecules of water of hydration per molecule of sodium sulfide.

The organic amides used in the method of this invention should be substantially liquid at the reaction temperatures and pressures employed. The amides can be cyclic or acyclic and can have 1 to about 10 carbon atoms per molecule. Examples of some suitable amides include formamide, acetamide, N-methylformamide, N,N-dimethylformamide, N,N-dimethylacetamide, N-ethylpropionamide, N,N-dipropylbutyramide, 2-pyrrolidone, N-methyl-2-pyrrolidone, ϵ -caprolactum, N-methyl- ϵ -caprolactum, N,N'-ethylenedi-2-pyrrolidone, hexamethylphosphoramide, tetramethylurea, and the like, and mixtures thereof.

Although the mole ratio of bis(p-chlorophenyl)sulfone to alkali metal sulfide can vary over a considerable range, generally it will be within the range of from 0.9:1 to 2:1, preferably from 0.95:1 to 1.2:1. The amount of organic amide can vary greatly, but usually will be within the range of from 100 grams to 2500 grams per gram-mole of alkali metal sulfide.

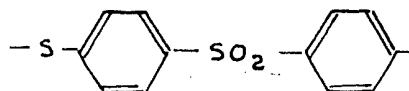
Although the reaction temperature at which the polymerization is conducted can vary over a considerable range, usually it will be within the range of from 150°C to 240°C, preferably from 180°C to 220°C. The reaction time can vary widely, depending in part on the reaction temperature, but generally will be within the range of from 10 minutes to 3 days, preferably from 1 hour to 8 hours. The pressure should be sufficient to maintain the bis(p-chlorophenyl)sulfone and organic amide substantially in the liquid phase.

The aromatic sulfide/sulfone polymers produced by the process of this invention can be separated from the reaction mixture by conventional procedures, e.g., by filtration of the polymer, followed by washing with water, or by dilution of the reaction mixture with water, followed by filtration and water washing of the polymer. If desired, at least a portion of the washing with water can be conducted at an elevated temperature, e.g., from 130°C to 250°C.

The aromatic sulfide/sulfone polymers produced by the process of this invention can be blended with fillers, pigments, extenders and other polymers. They can be cured through crosslinking and/or chain extension, e.g., by heating at temperatures up to 480°C in the presence of free oxygen-containing gas, to provide cured products having high thermal stability and good chemical resistance. They are useful in the production of coatings, films, moulded objects, and fibers.

EXAMPLES.

In Examples I and II, values for inherent viscosity were determined at 30°C in a 3:2 mixture, by weight, of phenol, and 1,1,2,2-tetrachloroethane at a polymer concentration of 0.5g/100 ml solution. In Examples III and IV, values for inherent viscosity were determined at 206°C in 1-chloronaphthalene at a polymer concentration of 0.4g/100 ml solution. In each of the Examples, values for glass transition temperature (T_g) and crystalline melting point (T_m), where shown, were determined on premelted and quenched polymer samples by differential thermal analysis. The values for polymer-melt temperature (PMT) were determined by placing portions of the polymer on a heated bar with a temperature gradient. The name poly(p-phenylene sulfide/sulfone) is used to describe an aromatic sulfide/sulfone polymer having recurring



units in the polymer molecule.

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Example I.

In a control run outside the scope of this invention, employing a dehydration step, 65.2 g (60 percent assay, 0.5 mole) sodium sulfide 0.2g sodium hydroxide (to react with sodium bisulfide and sodium thiosulfate present in trace amounts in the sodium sulfide), and 158.3g N-methyl-2-pyrrolidone were charged to a stirrer-equipped, 1-liter autoclave, which was then flushed with nitrogen. Dehydration of the mixture by heating to 205°C yielded 16 ml of distillate containing 14.1g water. To the residual mixture were charged 143.6g (0.5 mole) bis(p-chlorophenyl) sulfone and 40g N-methyl-2-pyrrolidone. The resulting mixture was heated for 5 hours at 200°C at a pressure of 40—55 psig. The reaction product was washed repeatedly with hot water and dried at 80°C under nitrogen in a vacuum oven to obtain a yield of 121.9g of amorphous poly(p-phenylene sulfide/sulfone) having an inherent viscosity of 0.29, a T_g of 203°C, and a PMT of 275°C.

Example II.

In a run within the scope of this invention, without the use of a dehydration step as employed in Example I, 65.2g (60 percent assay, 0.5 mole) sodium sulfide, 0.2g sodium hydroxide (to react with sodium bisulfide and sodium thiosulfate present in trace amounts in the sodium sulfide), 198.3g N-Methyl-2-pyrrolidone, and 143.6g (0.5 mole) bis(p-chlorophenyl) sulfone were charged to a stirrer-equipped, 1-liter autoclave, which was then flushed with nitrogen. The resulting mixture was heated for 5 hours at 200°C at a pressure of 45—55 psig. The reaction product was washed repeatedly with hot water and dried at 80°C under nitrogen in a vacuum oven to obtain a yield of 109.5g of amorphous poly(p-phenylene sulfide/sulfone) having an inherent viscosity of 0.36, a T_g of 209°C, and a PMT of 275°C.

Thus, based on inherent viscosity, the poly(p-phenylene sulfide/sulfone) produced in this Example was of substantially higher molecular weight than that produced in Example I, in which a dehydration step was employed prior to the polymerization step.

Example III.

In a run outside the scope of this invention, employing a dehydration step in the preparation of poly(p-phenylene sulfide) instead of poly(p-phenylene sulfide/sulfone), 127.2g (61 percent assay, 1.0 mole) sodium sulfide and

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276.7g N-methyl-2-pyrrolidone were charged to a stirrer-equipped, 1-liter autoclave, which was then flushed with nitrogen. Dehydration of the mixture by heating to 215°C yielded 22 ml of distillate containing 21.2g water. To the residual mixture were charged 149.9g (1.02 moles) p-dichlorobenzene and 50g N-methyl-2-pyrrolidone. The resulting mixture was heated for 3 hours at 245°C at a pressure of 20—100 psig. The reaction product was washed with hot water and dried to obtain a yield of 100.8g of poly(p-phenylene sulfide) having an inherent viscosity of 0.16, a T_g of 85°C, a T_m of 288°C, and a PMT of 271°C.

Example IV.

In a run outside the scope of this invention, comparable to the run in Example III except that a dehydration step was not employed prior to the polymerization step, 127.2g (61 percent assay, 1.0 mole) sodium sulfide, 326.7g N-methyl-2-pyrrolidone, and 149.9g (1.02 moles) p-dichlorobenzene were charged to a stirrer-equipped, 1-liter autoclave, which was then flushed with nitrogen. The resulting mixture was heated for 3 hours at 245°C at a pressure of 120—175 psig. The reaction product was washed with hot water and dried to obtain a yield of 92.2g of poly(p-phenylene sulfide) having an inherent viscosity of 0.12, a T_g of 71°C, a T_m of 285°C, and a PMT of 275°C.

Thus, the observation that use of a dehydration step in the preparation of poly(p-phenylene sulfide), as in Example III, resulted in a polymer of higher molecular weight than that obtained without the dehydration step, as in Example IV, rendered surprising the opposite effect subsequently observed in the preparation of poly(p-phenylene sulfide/sulfone), as illustrated in Examples I and II.

WHAT WE CLAIM IS:—

1. A process for the production of aromatic sulfide/sulfone polymers, which comprises reacting together, in the presence of an organic amide, a dihalo aromatic sulfone and an alkali

metal sulfide, other than lithium sulfide, wherein the dihalo aromatic sulfone is bis(p-chlorophenyl)sulfone and wherein there is present in the reaction medium water provided as water of hydration of the sulfide and optionally as free water.

2. A process according to claim 1, wherein the amide is an acyclic or cyclic amide containing from 1—10 carbon atoms.

3. A process according to claim 2, wherein the amide is N-methyl-2-pyrrolidone.

4. A process according to any one of the preceding claims, wherein the reaction medium contains from 1—10 moles of water per mole of alkali metal sulfide.

5. A process according to claim 4, wherein said amount of water is from 2—9 moles per mole of sulfide.

6. A process according to any one of the preceding claims, wherein the sulfide is hydrated sodium sulfide containing about 40% by weight of water of hydration.

7. A process according to any one of the preceding claims, wherein the reaction is carried out in the liquid phase at a temperature of from 180°—220°C.

8. A process according to any one of the preceding claims, wherein the mole ratio of aromatic sulfone to alkali metal sulfide is from 0.9:1 to 2:1.

9. A process according to claim 8, wherein said ratio is from 0.95:1 to 1.2:1.

10. A process according to any one of the preceding claims, wherein the amount of amide is from 100—2500 gms. per gm. mole of alkali metal sulfide.

11. A process according to claim 1, as hereinafter described in Example II.

12. Aromatic sulfone polymers prepared by a process as claimed in any one of the preceding claims.

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