



PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in Polymers

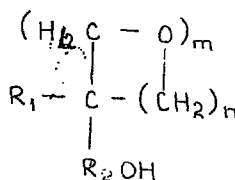
We, CELANESE CORPORATION formerly known as Celanese Corporation of America, of 522 Fifth Avenue, New York 36, State of New York, United States of America, a company incorporated in accordance with the laws of the State of Delaware, United States of America, do hereby declare the invention, for which 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 polymers and particularly to tough, high molecular weight, mouldable oxymethylene polymers.

Solid thermoplastic oxymethylene polymers may be prepared by polymerising a source of oxymethylene units, e.g. trioxane or formaldehyde. Oxymethylene copolymers of improved thermal stability may be prepared by introducing into the polymer chains groups which are resistant to thermal detachment, more particularly interspersed oxyalkylene units with adjacent carbon atoms which form links in the polymer chains. Such groups may be unsubstituted oxyalkylene units, e.g. oxyethylene units, derived from cyclic ethers such, for instance, as ethylene oxide or dioxolane, or may be substituted oxyalkylene units derived from lactones, carbonates, cyclic acid anhydrides or ethylenically unsaturated compounds, such, for instance, as styrene, divinyl ether, vinyl acetate, vinyl methyl ketone or acrolein. The polymers and copolymers may be end-capped by acylation or etherification after polymerisation or during polymerisation by use of selected chain transfer agents to increase their thermal stability which, in the case of the copolymers referred to, can also be increased by controlled degradation to eliminate terminal oxymethylene groups until the terminal groups of the polymer chains are those having adjacent carbon atoms.

The present invention is concerned with certain novel oxymethylene copolymers of the

general type referred to above. The copolymers of the invention consist as to at least 80% by weight of recurring oxymethylene groups and contain, dispersed among the oxymethylene groups, oxyalkylene groups having adjacent carbon atoms forming links in the polymer chains, some at least of the latter oxyalkylene groups being derived from molecules of an oxacyclic compound having a substituent alkylol group, in particular by ring scission between a carbon atom and an oxygen atom in a compound of the formula



wherein n is an integer from 0 to 2, m is 1 or 2, R₁ is hydrogen or an alkyl or alkylol group containing from 1 to 10 carbon atoms and R₂ is an alkylene radical having from 1 to 10 carbon atoms.

The preferred method of making the novel oxymethylene copolymers of the invention is by the copolymerisation of trioxane with a compound of the above formula in presence of boron fluoride or a boron fluoride complex.

For some applications, polymers are needed which exhibit rigidity combined with processability at high pressures, a combination of properties associated with a low melt index and a high 10x/1x melt index ratio.

The melt index, as used in this specification, is determined by heating a sample of a polymer in a 2 inch diameter cylinder to a temperature of 190°C. and forcing it under a load of 2.160 kg. applied by a piston of 0.373 inch diameter through an orifice of 0.0825 inch diameter and 0.315 inch long and is the

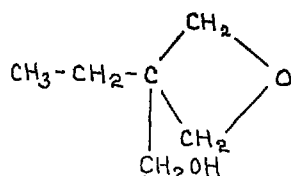
weight in grams of the polymer passing through the orifice in 10 minutes. The test is described in detail in ASTM D-1238-57T. The 10x melt index is generally used when melt index values are low and is determined in an identical manner except that the load is increased tenfold to 21.60 kg.

The preparation of rigid low melt index polymers in the past has required the use of feed materials of exceptionally high purity since impurities tend to act as chain terminators in polymerisations and lead to polymers of low molecular weight and high melt index. Moreover, prior polymers of relatively low melt index are difficult to process in that they usually have an extremely narrow temperature range of processability. By means of the invention it has been found possible to obtain, without using starting materials of exceptionally high purity, rigid copolymers which are of low melt index and high 10x/1x melt index ratio and which can be processed over a conveniently wide temperature range. Thus, copolymers can be obtained with melt indices so low as to be difficult to measure with accuracy, e.g. 2 to 5, 10x melt indices above 100 and 10x/1x melt index ratios between 35 and 90.

It seems likely that the properties of the novel copolymers are attributable to limited cross-linking between polymer molecules at the sites of the hydroxyl groups of the alkylol substituents referred to. Certainly, for the production of such readily processable polymers it is necessary to restrict the proportion of the groups containing an alkylol substituent to not more than 7% by weight of the polymer and preferably to less than 1, e.g. between 0.05 and 0.80, per cent by weight of polymer. With increasing content of such groups above 7% the polymer becomes progressively more intractable and no longer useful as a thermoplastic moulding material but useful in the role of thermosetting materials, i.e. for forming as shaped articles during the actual polymer production.

Preferably, the copolymers of the invention contain, in addition to the oxymethylene groups and groups derived from the alkylol-substituted oxacyclic compounds, other oxyalkylene units with adjacent carbon atoms which form links in the polymer chains such as those mentioned earlier and particularly oxyethylene units.

The preferred alkylol-substituted oxacyclic compound is trimethylolpropane oxetane, also known as 3-ethyl-3(hydroxy methyl) oxetane, which has the following structure:—



Other suitable alkylol-substituted oxacyclic compounds which may be used include trimethylolethane oxetane, 3-propyl-3(hydroxy methyl) oxetane, 3-butyl-3(hydroxy methyl) oxetane, 3-pentyl-3(hydroxy methyl) oxetane, 3-n-octyl-3(hydroxy ethyl) oxetane, 3-ethyl-3(hydroxy pentyl) oxetane, 3-hydroxy methyl oxetane, 3-ethyl-3-(hydroxy propyl) oxetane, 3-ethyl-3(hydroxy butyl) oxetane, hydroxy propyl glycidyl ether, pentaerythritol-monoformal, 3,3-dihydroxy ethyl oxetane, 3-ethyl-3(hydroxy ethyl) 1,5-dioxane and 3-ethyl-3(hydroxy methyl) tetramethylene oxide.

The copolymers are, as already indicated, preferably made by copolymerising trioxane and the alkylol-substituted oxacyclic compound in presence of boron fluoride or a boron fluoride complex. The proportions of the comonomer used to yield the readily processable copolymers may, in general, be equal to the proportion in the polymer of the groups it is desired to introduce by means of the comonomer. Where the copolymer is made from trioxane and the alkylol-substituted oxacyclic compound alone, it is preferred that this proportion should be such as to yield a polymer of which 93 to 99.5% by weight consists of oxymethylene groups while, with terpolymers, it is preferable to use proportions of monomers which yield a polymer containing at least 78% by weight of oxymethylene groups. The terpolymers which are above all preferred contain, by weight, 96.1 to 97.9% of oxymethylene groups, 2.0 to 2.9% of oxyethylene groups and 0.05 to 0.80% of groups derived from the alkylol-substituted oxacyclic compound.

While the boron fluoride co-ordination complexes with compounds in which oxygen or sulphur is the donor atom, e.g. complexes with ethers, esters, phenols and dialkyl sulphides, are generally satisfactory, the complex with dibutyl ether is preferred as catalyst. Any other means of catalysing the polymerisation of trioxane may, however, be used to assist the copolymerisation. Examples of substances which have been proposed for catalysing the polymerisation of trioxane include antimony trifluoride, antimony fluoroborate, bismuth trifluoride, bismuth oxyfluoride, nickelous fluoride, aluminium trifluoride, titanium tetrafluoride, manganous fluoride, manganic fluoride, mercuric fluoride, silver fluoride, zinc fluoride, ammonium bifluoride, phosphorous pentafluoride, hydrogen fluoride, thionyl chloride, fluorosulphonic acid, methane sulphonic acid, phosphorus trichloride, titanium tetrachloride, ferric chloride, zirconium tetrachloride, aluminium trichloride, stannic chloride and stannous chloride.

Where a boron fluoride-containing catalyst is used, it is usually present in the polymerisation zone in an amount such that its

boron fluoride content is between 0.0002 and 1.0 weight per cent based on the weight of the monomers in the polymerisation zone. Preferably, amounts between 0.003 and 0.03 weight per cent are used in continuous operation and between 0.0002 and 0.02% in a batch process.

The monomers in the reaction zone are preferably substantially anhydrous. Small amounts of moisture, such as may be present in commercial grade reactants or may be introduced by contact with atmospheric air, will not prevent polymerisation, but should be removed for best yields.

The temperature in the reaction zone may be, for instance, from 0°C. to 100°C. and the period of reaction from 5 minutes to 72 hours. Any desired pressure may be used, e.g. from sub-atmospheric to 100 atmospheres or more.

To control the molecular weight of the polymer product a small amount, e.g. from 100 to 3000 parts by weight per million parts by weight of trioxane, of a chain transfer agent, for instance methylal, may be included in the reaction mixture.

The polymerisation may be carried out in a solvent medium, e.g. cyclohexane, and the monomer mixture may, with advantage, be subjected to constant shearing during the polymerisation. Where boron fluoride or a complex thereof is used as catalyst, it is desirable to neutralise the catalyst when polymerisation is complete, since prolonged contact with the catalyst degrades the polymer. The polymerisation product may be treated with an aliphatic amine, e.g. tri-n-butyl-amine, in stoichiometric excess over the amount of free catalyst in the reaction product, and preferably in an organic wash liquid which is a solvent for unreacted trioxane. Alternatively, if desired, the reaction product may be washed with water which neutralises catalyst activity.

The novel copolymers, like other oxy-

methylene copolymers having interspersed carbon-to-carbon linkages, may be stabilised by removing terminal oxymethylene groups until a stable terminal group having a carbon-to-carbon linkage is reached by thermal or hydrolytic degradation.

The thermal degradation rate of the copolymers may also be reduced by the incorporation of conventional chemical stabilisers, for instance a combination of an anti-oxidant ingredient, e.g. a substituted bisphenol, and an ingredient to inhibit chain scission, e.g. a compound containing trivalent nitrogen.

In the Table below are set out the conditions used and results obtained in three Examples which are given to illustrate the invention. In the Examples trioxane, ethylene oxide and trimethylolpropane oxetane were charged in the amounts shown in the Table to a stainless steel vessel fitted with a sigma blade mixer. Cyclohexane and boron trifluoride di-n-butyl etherate catalyst (34.4 weight per cent BF_3) were also charged in the proportions shown. The reactions were initiated at 65°C. and the temperatures varied during the reaction as shown, the values given being the peak and final temperatures.

In Example 2 a second portion of catalyst was added dissolved in cyclohexane, thereby decreasing the trioxane to cyclohexane ratio from 20 to 16.

The figures for catalyst concentration are parts of boron fluoride per million parts of trioxane, by weight.

Before determining its properties the washed and dried polymer was stabilised by milling it with cyanoguanidine (0.1%) and 2,2'-methylene bis - 4 - (methyl - 6 - tertiary butyl phenol) (0.5%) for one hour at 210°C. under a nitrogen blanket in a plastograph. $K_D 230$ is the degradation rate, i.e. percentage weight loss per minute when heated in a circulating air oven at 230°C.

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TABLE

Example No.	1	2	3
Trioxane (parts by weight)	100	100	100
Trioxane to Cyclo- hexane Ratio	20:1	20—16:1	16:1
Ethylene Oxide (parts by weight)	2.0	2.0	2.0
Trimethylolpropane Oxetane (parts by weight)	0.25	0.50	0.50
Catalyst Concentration	75	75—100	75
Reaction Temperature Range (°C.)	91—27	83—30	92.5—35
Time Interval - Initiation to Peak Temperature (min.)	8.5	19	19
Duration of Run (min.)	22	40	32
Yield (%) on total monomers	85	82	85
Weight Loss in Stabilisation (%)	13	20	19
Melt Index (dg/min.)	5.3	13.9	2.66
10x Melt Index (dg/min.)	210	770	178
10x/1x Ratio	40	56	67
K _{D 230}	0.027	0.049	0.019

- 5 The readily processable copolymers such as those produced according to the Examples, besides being thermoplastic, are soluble in the usual solvents for oxymethylene polymers. For example, the finely divided polymers will dissolve in p-chlorophenol to the extent of at least 0.1 weight per cent at 60°C. and are substantially completely soluble in a solvent containing 60 weight per cent of methanol and 40 weight per cent of water when heated with the solvent to a temperature of 160°C. The copolymers have melting points of at least 150°C. and are normally millable at a temperature of 200°C. They have a number average molecular weight of at least 10,000 and, besides having high thermal stability as shown by the figures given in the Examples, exhibit high alkaline stability. For example, if the chemically stabilised copolymers are refluxed at a temperature of about 145°C. in a 50% solution of sodium hydroxide in water for a

period of 45 minutes, their weight will be reduced by less than 1%.

These copolymers also exhibit high melt elasticities and are therefore exceptionally suitable for blow moulding, and vacuum forming. High melt elasticity in a polymer causes it to thicken and foreshorten as it is extruded under heat and pressure from a constricted orifice. In blow moulding this tendency to thicken and foreshorten in a descending parison partially counteracts the effect of gravity on the parison and makes it possible for a larger parison to be maintained without increasing internal stresses caused by the increased weight. It is convenient to express the melt elasticity as the percentage increase in extrudate diameter over orifice diameter when the polymer is extruded under the conditions used when determining the melt index as described in ASTM D-1238-57T. Copolymers are commonly obtained according to the

invention with melt elasticities above 20% and even above 30%. For an oxymethylene homopolymer of comparable melt index or for a comparable copolymer containing no groups derived from alkylol-substituted oxacyclic compounds the melt elasticity is usually below 10%.

The copolymers have high melt strength and, accordingly, lend themselves to processing in such operations as, for example, the blow moulding of relatively large bottles and the extruding of intricate and large profiles, especially where good dimensional control is important. Thus in the extrusion of pipe, excellent control of surface pulsations and wall thickness may be maintained.

In a typical blow moulding operation, 4-ounce Boston round bottles may be prepared using a 2 inch extruder having a length/diameter ratio of 14/1, a die bushing internal diameter of 0.562 inch, a die mandrel outside diameter of 0.200 inch, a land length of 0.5 inch, a die temperature of 340°F. (171°C.), a melt temperature of 380°F. (193°C.), a mould temperature of 230°F. (110°C.) and a 20—22 second cycle.

In a typical extrusion operation, a 1 inch internal diameter pipe having a 0.08 inch wall may be extruded through a 2½ inch Davis Standard Extrusion Machine having a die bushing of 1.200 inches internal diameter and a die mandrel of 1.035 inches outside diameter, an external sleeve 9 inches long and of 1.235 inches internal diameter being situated adjacent the die bushing and concentric with it. The sleeve controls the outer diameter of the pipe while the inner diameter is controlled by the draw rate. A temperature of 400°F. (204°C.) may be maintained at the die and a temperature of 175°F. (80°C.) at the sleeve. Air pressure in the extruded pipe can be maintained at a gauge pressure of 23 pounds per square inch and the pipe taken up at a rate of 6½ feet per minute.

By copolymerising trioxane with more than 7% of its weight of the alkylol-substituted oxacyclic compound intractable, apparently cross-linked, copolymers may be obtained, the alkylol-substituted oxacyclic compound being used in amounts up to 20% by weight, based on the total monomer weight. In such copolymers, as in the readily processable copolymers, it is preferred to include as a third monomeric component, a compound having at least two adjacent carbon atoms such, for instance, as ethylene oxide or dioxolane. In accordance with this aspect of the invention, the copolymers are preferably composed of from 70% to 98.5% by weight of oxymethylene groups, from 0.5% to 10% by weight of the groups having adjacent carbon atoms and more than 7% and up to 20% by weight of groups derived from the alkylol-substituted oxacyclic compound.

Substantially intractable copolymers may be

formed into the desired shape prior to the completion of the polymerisation process. The polymerisation mixture may, for example, be heated and subjected to a shearing action for a limited period, sufficient to assure complete mixing, and thereafter transferred to a mould for shaping and for completion of the polymerisation reaction.

WHAT WE CLAIM IS:—

1. Oxymethylene copolymers consisting as to at least 80% by weight of recurring oxymethylene groups and containing, dispersed among the oxymethylene groups, oxyalkylene groups having adjacent carbon atoms forming links in the polymer chains, some at least of the latter oxyalkylene groups being derived from molecules of an oxacyclic compound having a substituent alkylol group.

2. Oxymethylene copolymers according to Claim 1, wherein the groups derived from said oxacyclic compound are derived from trimethylolpropane oxetane.

3. Oxymethylene copolymers according to Claim 1 or 2 and containing oxyethylene groups the carbon atoms of which form links in the polymer chains.

4. Oxymethylene copolymers according to Claim 1, 2 or 3, which are thermoplastic and contain not more than 7 weight per cent of groups derived from an oxacyclic compound having a substituent alkylol group.

5. Oxymethylene copolymers according to Claim 4 and containing from 0.05 to 0.80% by weight of the groups derived from said oxacyclic compound.

6. Process for the production of oxymethylene copolymers, which comprises copolymerising trioxane and up to 25% of its weight of an oxacyclic compound having a substituent alkylol group.

7. Process according to Claim 6, wherein the mixture subjected to polymerisation contains not more than 7% by weight of said oxacyclic compound.

8. Process according to Claim 7, wherein the mixture subjected to polymerisation contains between 0.05 and 0.80% by weight of said oxacyclic compound.

9. Process according to Claim 6, 7 or 8, wherein a terpolymer is produced by copolymerising trioxane, said oxacyclic compound and a third compound which introduces into the polymer groups having adjacent carbon atoms which form links in the polymer chains.

10. Process according to Claim 9, wherein said third compound is ethylene oxide or dioxolane.

11. Process according to any of Claims 6 to 10, wherein the polymerisation is carried out in presence of boron fluoride or a coordination complex thereof.

12. Process for the production of oxymethylene copolymers, substantially as hereinbefore described.

13. Process for the production of oxy-

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The copolymers have high melt strength and, accordingly, lend themselves to processing in such operations as, for example, the blow moulding of relatively large bottles and the extruding of intricate and large profiles, especially where good dimensional control is important. Thus in the extrusion of pipe, excellent control of surface pulsations and wall thickness may be maintained.

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3. Oxymethylene copolymers according to Claim 1 or 2 and containing oxyethylene groups the carbon atoms of which form links in the polymer chains.

4. Oxymethylene copolymers according to Claim 1, 2 or 3, which are thermoplastic and contain not more than 7 weight per cent of groups derived from an oxacyclic compound having a substituent alkylol group.

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6. Process for the production of oxymethylene copolymers, which comprises copolymerising trioxane and up to 25% of its weight of an oxacyclic compound having a substituent alkylol group.

7. Process according to Claim 6, wherein the mixture subjected to polymerisation contains not more than 7% by weight of said oxacyclic compound.

8. Process according to Claim 7, wherein the mixture subjected to polymerisation contains between 0.05 and 0.80% by weight of said oxacyclic compound.

9. Process according to Claim 6, 7 or 8, wherein a terpolymer is produced by copolymerising trioxane, said oxacyclic compound and a third compound which introduces into the polymer groups having adjacent carbon atoms which form links in the polymer chains.

10. Process according to Claim 9, wherein said third compound is ethylene oxide or dioxolane.

11. Process according to any of Claims 6 to 10, wherein the polymerisation is carried out in presence of boron fluoride or a coordination complex thereof.

12. Process for the production of oxymethylene copolymers, substantially as hereinbefore described.

13. Process for the production of oxy-

methylene terpolymers, substantially as described in any of the Examples.

14. Oxymethylene copolymers whenever produced by any of the processes claimed in
5 Claims 6 to 13.

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* C L M S *

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