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(54) IMPROVEMENTS IN OR RELATING TO
CATIONIC POLYMERISATION

(71) I, THE SECRETARY OF STATE FOR DEFENCE, LONDON, 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:—

5 The present invention relates to the initiation of cationic polymerisation and especially to the use of cationic polymerisation initiators in the production of block copolymers, that is copolymers wherein the units derived from a single monomer occur within the polymer chain in significant groups, generally of more than about 4 units. 5

10 Block copolymers are widely used where it is required to combine the characteristic properties of two or more different polymer systems in a single material. For example butadiene/styrene block copolymers display properties normally associated with synthetic rubber (polybutadiene) and also those associated with thermoplastics (polystyrene). These "thermoplastic elastomers", which may be repeatedly moulded, may be used, for example, tyres for low speed 15 vehicles. Similarly epoxide adhesives may be flexibilised by the inclusion within the molecule of polybutadiene units. 10

20 Where the two monomers involved are capable of being polymerised by the same type of chain reaction, which may be anionic, cationic or free radical, block copolymers may often be produced by homopolymerisation of one monomer followed by addition of the second monomer before the homopolymer is chain stopped. This technique is particularly suitable in anionic systems where the so-called "living polymers" may be kept for considerable periods under suitable 25 conditions, but is not generally applicable to cationic and free-radical systems where termination and transfer reactions occur readily, resulting in considerable amounts of homopolymer being produced. 25

30 In other cases it is necessary to polymerise the monomers by different techniques either because they will not polymerise by a common route or because the product would not be in the desired form (for example, anionic polybutadiene can be prepared chiefly 1:2 linked whilst the free-radical product is predominantly 1:4). In such cases the desired block copolymer may be produced by forming homopolymer blocks from one comonomer and terminating these with a unit which is capable of initiating a different type of polymerisation with the second 35 monomer. For example, homopolymer blocks may be produced by anionic or free-radical polymerisation and after suitable termination may be used as the basis for cationic polymerisation initiated by the process of the present invention. 35

40 According to the present invention, a process for the cationic polymerisation of a monomer comprises the steps of (a) preparing an organic salt of an active gegenanion (as herein defined) by reacting a polymeric organic halide with a metal salt of the anion in a solvent which causes the corresponding metal halide to be precipitated, said organic salt containing a carbonium ion which initiates polymerisation of said monomer; and (b) reacting said monomer with the organic salt in said solvent to produce a polymeric chain of the desired length. 40

45 The term "active gegenanion" as used herein denotes those anions which, in the form of the free acid, are known to be capable of initiating cationic polymerisation. Such anions normally form strong acids and are typically large complex anions bearing a single charge which therefore display low nucleophilicity. That is, they are not so closely associated with the carbonium 45

counter-ion as to prevent addition of monomer. Examples of suitable anions include perchlorate, tetrafluoroborate, hexafluoroantimonate, hexachloroantimonate, trifluoroacetate, hexafluorophosphate and hexafluorosilicate anions.

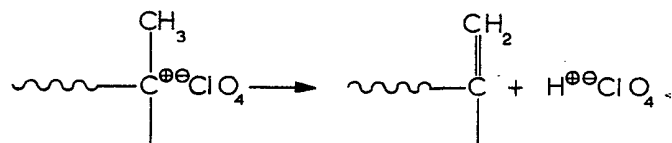
The metal cation used in the preparation of the organic salt should be one whose halide salt corresponding to the halogen in the organic halide is insoluble in the solvent system chosen. The reaction proceeds by precipitation of the metal halide to leave the anion and the carbonium ion which initiates polymerisation of the monomer. The preferred salts are silver salts, conveniently silver perchlorate.

The organic halide and metal salt may be reacted to give the organic salt either before or after addition of the monomer to one or both of them. The reaction will normally be carried out in a conventional solvent for cationic polymerisation, for example, hexane, benzene, toluene, methylene chloride or mixtures of these. In certain cases, however, the monomer itself may act as solvent, for example tetrahydrofuran. The temperature may vary over a wide range depending on the monomer and solvent used but will generally be from +30°C to -100°C, particularly from +25°C to -5°C.

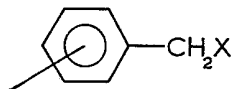
The monomer may be any monomer capable of polymerisation by the cationic route, for example, styrene, α -methyl styrene, isoprene, vinyl ethers, N-vinyl carbazole, acenaphthalene, isobutylene or a cyclic oxide or sulphide such as tetrahydrofuran, ethylene oxide, propylene oxide, butylene oxide, caprolactone or thietane.

The organic halide may be a chloride or iodide or possibly a fluoride, but is preferably a bromide. It may be halide-terminated polymer, for example as produced by "killing" (terminating) an anionic living polymer with a dihalide or excess of a halogen. In either case the carbonium ion generated from the organic halide may have a single positive charge on a terminal carbon atom or may have at least two positive charges on terminal carbon atoms. In the case of the halide-terminated polymer this means that the polymer may have halide groups at one or both ends of the polymer chain. Generally a monohalide polymer will produce a predominantly A—B type block copolymer (where A represent a block derived from the halide-terminated polymer and B a block derived from the second monomer) whilst a dihalide polymer will produce a predominantly B—A—B type copolymer. The halide-terminated polymer may itself be a preformed block copolymer, and the product of the present process will then be a more complex block copolymer. A further variety of organic halide is provided by a polymeric species having non-terminal halogen atoms, i.e. halogen atoms dispersed along its length. Such a species is exemplified by a polyvinyl halide, for example polyvinyl chloride. In the case of such organic halides, the carbonium ion produced in the present process will be a polymeric species having at least one positive charge on a non-terminal carbon atom and the product will be a polymeric main chain with a polymeric side chain or chains distributed along its length. Again in this case, the polymeric halogen-containing species may itself be a block copolymer.

Preferably the organic halide should not contain a hydrogen atom on a carbon atom adjacent that bearing the halide, since such an α -hydrogen atom may participate in a side reaction to eliminate a hydrogen and destroy the carbonium ion, e.g.:—



Although the resulting perchloric acid may itself initiate cationic polymerisation, the organic residue of the halide will not be incorporated and hence two homopolymers will be produced instead of a block copolymer. Hence the organic halide is preferably a polymer terminated by the group



wherein X represents a halogen, especially bromine.

The metal salt and the organic halide are clearly preferably used in equivalent amounts, that is about equimolar for a monohalide and 2:1 molar ratio for a

dihalide. An excess of metal salt will normally have no disadvantage, except cost, but a deficiency will generally be undesirable.

Model systems to illustrate the polymerisation reaction of the invention will now be demonstrated by the following examples using non-polymeric halides.

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EXAMPLE 1

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0.31 gm benzyl chloride (2.4 m moles) were added to a solution of 0.5 gm silver perchlorate (2.4 m moles) in 20 ml benzene, resulting in the gradual formation of a white precipitate. 10 gm acenaphthalene (66 m moles) dissolved in 14 ml benzene was added. The brown mixture was stirred for 1 hour whilst maintained at room temperature, by cooling when necessary. A few ml of methanol were added and the mixture filtered to remove silver chloride. The filtrate was added to an excess of methanol and filtered to separate the precipitated polymeric product. The yield of polymer was 8.7 grms (87% of theoretical).

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EXAMPLE 2

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0.5 gm silver perchlorate (2.4 m moles) were dissolved in 30 ml benzene/10 ml methylene chloride, and cooled to 0°C. A solution of 0.33 gm α,α' -dibromo-p-xylene (1.7 m moles) in 7 ml benzene was added, forming a pale yellow precipitate. 10 gm styrene (100 m moles) were added, and the mixture stirred for 1 hour at 0°C. A few ml of water were added and the mixture filtered. The filtrate was added to an excess of methanol and the product filtered off giving a yield of 7.35 gm of polymer (74%).

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EXAMPLE 3

(Comparative Example)

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Example 2 was repeated using toluene as solvent and omitting the α,α' -dibromo-p-xylene. No polymer was formed indicating that the dibromide is involved in the reaction.

EXAMPLE 4

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0.34 gm crotyl bromide (2.4 m moles) were added to a solution of 0.5 gm silver perchlorate (2.4 m moles) in 50 ml toluene at 0°C. A white precipitate formed instantly. The mixture was cooled to -78°C and 11.8 gm α -methyl styrene (100 m moles) added. The orange solution was stirred at -78°C for 1 hour. A few ml of methanol were added resulting in removal of the orange colour. The reaction mixture was filtered and added to an excess of methanol to precipitate the polymer product which was then filtered off. A yield of 6.5 gm polymer was obtained (55%).

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EXAMPLE 5

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0.34 gm benzyl bromide (2.0 m moles) was added to a solution of 0.68 gm silver hexafluoroantimonate (2.0 m moles) in 29 gm tetrahydrofuran (400 m moles). A white precipitate formed instantly. The mixture became fairly viscous after four hours at room temperature. The polymer was extracted from the reaction mixture with ether and the extract washed with brine. The ether extract yielded 6.5 gm of polymer (23% of theoretical).

EXAMPLE 6

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0.46 gm 1-bromoethyl benzene (2.4 m moles) were added to a solution of 0.5 gm silver perchlorate (2.4 m moles) in 25 ml toluene and 35 ml methylene chloride at 0°C. A white precipitate was produced. A mixture was cooled to -78°C and 28.8 gm vinyl ethyl ether (400 m moles) added dropwise over a period of 45 minutes. The reaction was exothermic, and a black colour was produced by the addition of monomer. After stirring for a further hour, the mixture had become very viscous. The addition of methanol and sodium hydroxide solution destroyed the colour. The mixture was filtered, stripped of solvent and extracted with water/tetrahydrofuran. The THF layer was dried and evaporated giving 28.4 gm orange viscous material (99% yield).

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EXAMPLE 7

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0.3 gm allyl bromide (2.4 m moles) were added to a solution of 0.5 gm silver perchlorate (2.4 m moles) in 30 ml benzene/10 ml methylene chloride, at 0°C. A white cloudy precipitate formed. 10.4 gm styrene (100 m moles) were added

slowly. After stirring for 1 hour at 0°C a solution of lithium chloride in methanol was added to terminate the reaction and precipitate excess silver. The mixture was filtered to remove silver salts and precipitated into methanol. 71 grms of white polymer was obtained (68% yield).

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EXAMPLE 8
(Comparative example)

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Example 7 was repeated omitting the allyl bromide and stirring for 2 hours instead of 1 hour. No polymer was produced.

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EXAMPLE 9

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Example 7 was repeated using 9,10-dichloromethylanthracene in place of allyl bromide and toluene as solvent in place of benzene/methylene chloride. A 14% yield of polymeric product was obtained.

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EXAMPLE 10

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0.33 gm α,α' -dibromo-p-xylene (1.7 m moles) in 10 ml benzene were added to 0.5 gm silver perchlorate (2.4 m moles) dissolved in 25 ml benzene/10 ml methylene chloride, forming a pale yellow precipitate. 13.6 gm isoprene (200 m moles) were added very slowly, maintaining the reaction at 0°C. The reaction was exothermic. Stirring was continued for a further 3 hours. A few ml of methanol were added and the solution was filtered and then precipitated into methanol. 2.33 gm of viscous product was obtained on filtration (17% yield). The methanol solution was evaporated and extracted with aqueous ether. A further 11.6 grms of material was obtained (83% yield).

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EXAMPLE 11

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0.5 gm 1-bromoethyl benzene (2.7 m moles) were added to a solution of 0.5 gm silver perchlorate (2.4 m moles) in 25 ml benzene/10 ml methylene chloride, at 0°C. 9.5 gm N-vinyl carbazole (50 m moles) were dissolved in 10 ml of methylene chloride and added slowly to the reaction mixture. A rust colour was produced, and the mixture became very viscous. 10 ml of benzene were added. After stirring for $\frac{1}{2}$ hour at 0°C the reaction mixture was transferred to a beaker containing ammonia solution. Tetrahydrofuran was added and the mixture stirred. The silver bromide was dissolved by the ammonia solution and the polymer went into the organic phase. After washing with brine the organic phase was precipitated into methanol to give a yield of 9.4 gm white powder. (100% yield). The product was not completely soluble in tetrahydrofuran.

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The following examples illustrate the process of the present invention as applied to polymeric halides to produce block copolymers.

EXAMPLE 12

Preparation of a Styrene/Tetrahydrofuran A—B Block Copolymer.

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Polystyrene, molecular weight 2000 and terminated at one end by bromine, was prepared by adding a solution of "living" polystyrene, (initiated by n-butyl lithium in benzene/THF solvent), to an excess of molecular bromine.

The polymer was isolated by precipitation into methanol.

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2 gm of the above bromine-terminated polystyrene was reacted with 0.2 gm of silver perchlorate in 20 ml tetrahydrofuran. A white precipitate of silver bromide was formed on mixing after which the mixture was maintained at 78°C for 4 days followed by 1 day at room temperature. The viscous reaction product was extracted with ether and washed with brine to yield 10 gm of a colourless viscous liquid.

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Comparison of the ultra-violet and refractive index detector traces for the gel permeation chromatographs of the copolymer and the starting material, produced strong evidence for the presence of block copolymer containing both styrene and tetrahydrofuran units.

EXAMPLE 13

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Preparation of an α -methyl Styrene/Tetrahydrofuran A—B—A Type Block Copolymer

A polymer of molecular weight about 8,000 was made by reacting "living" α -methyl styrene tetramer with excess α,α' -dibromo-p-xylene, to give a polymer

terminated at both ends by bromine. The polymer was extracted by precipitation into methanol.

2.0 gm of the above polymer was dissolved in 20 ml tetrahydrofuran and added to a stirred solution of 0.2 gm silver perchlorate in 10 ml tetrahydrofuran. A white precipitate of silver bromide formed immediately. After 3 days at room temperature the mixture became viscous. The polymer was extracted with methylene chloride and washed with brine. 7 gm of a yellowish rubbery material was obtained. GPC analysis showed the presence of block copolymer.

EXAMPLE 14

Preparation of a Butadiene/Tetrahydrofuran A—B—A Type Block Copolymer.

Polybutadiene, molecular weight about 10,000 and terminated at both ends by bromine, was prepared by adding a solution of "living" polybutadiene, (initiated by lithium naphthalene in tetrahydrofuran) to an excess of m-xylene dibromide. The polymer was extracted with pentane.

0.36 gm of the above product was reacted with 0.2 gm of silver perchlorate in 50 ml tetrahydrofuran. A white precipitate of silver bromide was produced. After 4 days at room temperature the mixture had become very viscous. The polymer was extracted with ether and washed with brine. The ether solution was dried with magnesium sulphate and evaporated to give 7.2 gm of rubbery product.

Gel permeation chromatography, showed the formation of block copolymer.

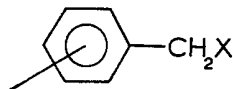
WHAT WE CLAIM IS:—

1. A process for the cationic polymerisation of a monomer which comprises the steps of (a) preparing an organic salt of an active gegenanion (as herein defined) by reacting a polymeric organic halide with a metal salt of the anion in a solvent which causes the corresponding metal halide to be precipitated, said organic salt comprising a carbonium ion which initiates polymerisation of said monomer; and (b) reacting said monomer with the organic salt in said solvent to produce a polymeric chain of the desired length.

2. A process as claimed in claim 1, wherein the carbonium ion has one positive charge on a terminal carbon atom.

3. A process as claimed in claim 1, wherein the carbonium ion has at least two positive charges on terminal carbon atoms.

4. A process as claimed in claim 2 or claim 3, wherein the organic halide is a polymer terminated by at least one



group, where X represents a halogen atom.

5. A process as claimed in claim 1, wherein the carbonium ion is a polymeric species having at least one positive charge on a non-terminal carbon atom and the product is a polymeric species having at least one polymeric side chain derived from the monomer.

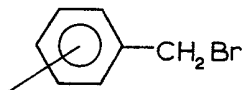
6. A process as claimed in claim 5, wherein the polymeric organic halide is a polyvinyl halide.

7. A process as claimed in claim 6, wherein the polyvinyl halide is polyvinyl chloride.

8. A process as claimed in claim 1, wherein the polymeric organic halide is an aliphatic or aromatic monohalide or dihalide.

9. A process as claimed in any of claims 1 to 5 and 8, wherein the halide is bromide.

10. A process as claimed in claim 9, wherein the organic salt is derived from a polymer terminated by the group



11. A process as claimed in any of the preceding claims, wherein the gegenanion is selected from the perchlorate, tetrafluoroborate, hexafluoroantimonate, hexachloroantimonate, trifluoroacetate, hexafluorophosphate and hexafluorosilicate anions.

12. A process as claimed in claim 2 or claim 3, wherein the polymeric organic halide is prepared by terminating an anionic living polymer with a dihalide or with an excess of a halogen.

5 13. A process as claimed in any of the preceding claims, wherein the metal cation in the metal salt of the gegenanion is silver. 5

14. A process as claimed in claim 13, wherein the metal salt is silver perchlorate.

10 15. A process as claimed in any of the preceding claims which is carried out in a solvent comprising hexane, benzene, toluene, methylene chloride or mixtures thereof. 10

16. A process as claimed in any of claims 1 to 15, wherein the reaction is carried out at a temperature of from +30°C to -100°C.

17. A process as claimed in claim 16, wherein the reaction is carried out at temperature of from +25°C to -5°C.

15 18. A process as claimed in any of the preceding claims, wherein the monomer is styrene, α -methyl styrene, isoprene, vinyl ethers, N-vinyl carbazole, acenaphthalene, isobutylene, tetrahydrofuran, ethylene oxide, propylene oxide, butylene oxide, caprolactone or thietane. 15

19. A polymer when produced by the process of any of the preceding claims.

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Agent for the Applicants.

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