

A PROCESS FOR THE PREPARATION OF AROMATIC
POLYISOCYANATE COMPOUNDS IN THE GASEOUS PHASE

This invention concerns a process for the preparation of aromatic compounds substituted by at least two isocyanate groups, more particularly, toluene diisocyanate and its isomers, either alone or as a mixture.

The preparation of aromatic compounds substituted by one or more isocyanate groups by the reaction of amines with phosgene in the gaseous phase is well known, although it has only been of real value in the transformation of monofunctional amines.

The major drawback of known processes for the production of aromatic polyisocyanates is that they use very large quantities of phosgene compared with the amines used in the reaction. The formation of polyisocyanates from the corresponding polyamines requires an excess of phosgene of the order of 200 to 300 mole% with respect to the amine functions. This excess of phosgene is known to increase the phosgenation rate. Furthermore, it prevents the formation of undesirable side-products resulting from the reaction of the amine with the isocyanate and which, apart from reducing the yield of polyisocyanate formed, also frequently suffer from the problem of being solid and thus blocking the reactors. These problems do not exist when the amines used are aliphatic or aromatic monoamines or aliphatic polyamines.

However, while large excesses of phosgene are recommended for reaction efficiency, working with such quantities is undesirable from the safety stand-point because of the toxicity of this reactant and the constraints imposed on the use thereof. These constraints are all the more severe when larger amounts of phosgene are used in the installation.

A further feature of processes involving the reacting of polyamines with phosgene in the gaseous phase resides in the need to increase the efficiency of the mixing between the reactants in order to avoid side reactions and obtain good yields of polyisocyanates.

The use of reactors containing movable stirring means for the reaction mixture have thus been recommended. However, this method has problems linked to the use of rotating parts in the mechanical stirrer, in particular sealing at the rotation axis, problems with clogging and then blocking the movable stirrer due to the adhesion of products from side reactions.

EP-A-570,799 does not describe a reactor of the above type but requires injection of the reactants into a static mixing zone such that the residence time is 0.1 to 0.3 seconds and the degree of segregation between the reactants is 10^{-3} . Once homogenised, the reaction mixture enters the reaction zone proper, without retro-mixing, in which the flow is piston flow characterised by a minimal Bodenstein and/or Reynolds number. These features are essential because the description states that unless this is the case, the reactor can become blocked. The drawback with this type of process is that it requires the use of a large excess of phosgene of from 150 to 250 mole% with respect to the amine functions.

The present invention seeks to provide a process for the preparation of aromatic compounds substituted by at least two isocyanate groups which does not suffer from the above problems, in particular as regards the use of too much excess phosgene.

The present invention provides a process for the preparation of aromatic compounds substituted by at least two isocyanate groups, wherein at least one compound (A) comprising at least two primary amine functions and at least one aromatic group is brought into contact with an excess of phosgene, the phosgene being in excess by between 0 and 100% with respect to the number of moles of amine functions in compound (A), both reactants being introduced in the gaseous phase, in a mixed reactor comprising a first, homogenising zone corresponding to 20% to 80% of the total volume of the reactor, and a second zone in which the flow is close to piston flow, corresponding to 80% to 20% of the total volume of the reactor.

The preparation process of the invention can produce isocyanates corresponding to the transformation of the above

amines without the need to carry out the reaction in the presence of a very high excess of phosgene. We have established that phosgenation of aromatic polyamines can be effected under these conditions without the need for a prohibitive increase in reaction time. Furthermore, the isocyanate yield at the reactor outlet is as high as that obtained with processes using large excesses of phosgene.

An important advantage of the process of the invention is that it is no longer necessary to recycle the unreacted phosgene, in contrast to the processes using large excesses of this compound, which require such an operation in order to be economically viable. Avoiding the recycling of the phosgene has the advantage of doing away with a zone in the process which circulates a large quantity of concentrated phosgene, and which may also be under pressure, with all the associated safety constraints which this entails.

In a particular embodiment of the invention, the process is carried out with at least one compound (A) comprising at least two primary amine functions and at least one aromatic C₆-C₁₄, preferably C₆-C₁₀ group, which is unsubstituted or substituted by one or more linear, cyclic or branched, saturated or unsaturated C₁-C₁₀ hydrocarbon groups.

More precisely, the above hydrocarbon groups may, for example, be selected from alkyl, aryl, alkyl-aryl and aryl-alkyl C₁-C₁₀ hydrocarbon groups, preferably C₁-C₆ groups.

Preferably compound (A) has the formula:



wherein R represents an aromatic group such as one described above.

In a particular embodiment of the invention at least one compound (A) is used in which R is unsubstituted or substituted by one or more alkyl C₁-C₁₀ groups, preferably C₁-C₆ groups.

Particular examples of R are benzene and naphthalene nuclei which are unsubstituted or substituted by one or more methyl, ethyl, propyl, butyl, pentyl or hexyl groups and/or their isomers.

Preferably, the process is carried out using at least one compound (A) selected from toluene diamine, xylylene diamine, or phenylene diamine. These compounds can be used alone or as a mixture, with or without their isomers. More preferably, compound (A) is toluene diamine.

A particularly advantageous embodiment of the invention consists of carrying out the reaction in the presence of an excess of from 5 to 60 mole% of phosgene, with respect to the number of amine functions in compound (A).

The reactants brought into contact with each other in the process of the invention, i.e., at least one compound (A) and phosgene, can be used alone or in the presence of a diluent. The term "diluent" means a compound which is inert towards the reactants and products of the reaction under the reaction conditions.

In addition to inert gases, in particular nitrogen, the vapour of a solvent for compound (A) and/or phosgene can be used as a diluent. The solvent can be selected from benzene, xylene, ortho-dichlorobenzene, monochlorobenzene or any other solvent which is normally used in phosgenation reactions, provided that it is stable under the reaction conditions (e.g. temperature and residence time).

When compound (A) is dissolved in a diluent, it can in particular be present in a concentration by weight of from 3% to 30% in the diluent. This concentration is preferably from 10% to 20%.

Thus if a diluent is used with the amine, mixing preferably takes place before introduction of the reactants into the reactor. In general, the amine is first dissolved in its solvent in the liquid phase. The resulting mixture is then vaporised at the temperature required for reaction using any means known to the skilled person.

The reactants, optionally in the presence of a diluent, are brought into contact in the vapour phase. The reactants are preheated using any known means to produce vaporised products during their introduction into the reactor. Furthermore, the reaction is carried out under conditions which ensure that the reactants remain in the vapour state.

Normally, the preheating temperature for the reactants is of the same order as that required for carrying out the phosgenation.

In a preferred reactor, the first zone comprises a reactor whose length is of the same order of size as its cross section. For convenience, the reactor in this first zone is cylindrical in shape, though, of course, any other geometric form (e.g. cubic or spherical) with a cross section which is close to the length would be suitable.

In a preferred embodiment, the first zone corresponds to 40% to 80% of the total volume of the reactor.

The reactants are introduced under conditions in which the zone in the reactor closely corresponds to a homogenising reactor.

With this aim, introduction of the reactants must preferably occur so as to promote a turbulent area in this zone to provide good homogenisation of the reaction mixture.

Introduction can take place in a number of ways. Preferably, means are used which encourage retromixing of the reactants (or back mixing), for example by nozzles or multijet injectors.

Nozzles can, for example, be concentric, i.e., composed of two concentric tubes inserted one into the other forming a central portion and an annular portion. Compound (A) and the phosgene, optionally in the presence of a diluent, can be introduced into either the annular portion or via the central portion.

Multijet injectors can comprise either a system including a number of jets converging towards one or more central jets, or a number of jets located in different areas of the reactor with different spraying angles and directions to stir the gas streams.

Introduction of the reactants in the vapour phase can take place at any part of the stirred zone. Thus the reactants may be introduced into a region which is close to the wall up to a region close to the centre of the reactor.

The first zone may or may not include static systems (e.g. obstacles or baffles) which encourage retromixing of the reactants and homogenisation of the mixture.

The second zone of the reactor corresponds to a finisher for the phosgenation reaction. It also allows maximum conversion to be obtained while minimising the total volume of the reactor.

It comprises a reactor of a length which is greater than its cross section. Tube reactors are an example, although other geometric shapes would be suitable provided that the above condition is satisfied.

In a preferred embodiment of the invention, the second zone corresponds to 60% to 20% of the total volume of the reactor.

This reaction zone can also be lined with internal obstacles or baffles; preferably, it is not.

The reactor used to carry out the process of the invention preferably does not contain any movable mechanical stirrers, in either the first or second zone.

The reaction of the invention can be carried out in any type of reactor which is made from a material which is compatible with the operating conditions. In particular, the reaction can be carried out in a reactor made from glass or steel which may be alloyed or enamelled.

The residence time for the reactants in the reactor containing the two zones is, in particular, from 1.5 to 30 seconds. Preferably, the residence time is from 3 to 15 seconds. It should be noted that the residence time in one or other of the two zones is proportional to the distribution by volume of the two zones with respect to the whole.

We have surprisingly found that carrying out a non negligible portion of the reaction in a homogenising reactor does not cause the problems which would normally be expected, despite the use of a slight excess of phosgene.

This is all the more surprising since known processes recommend mixing the reactants in as short a time as possible, in order to avoid reaction. The reaction takes place in a different zone of the reactor, where the residence time is up to 10 times greater than that in the preceding zone. The zone in which the reaction proper takes place is characterised by the absence of retromixing of the reactants, which was felt to be the origin of blockages. The present

invention has shown that it is of no importance that the major portion of the phosgenation reaction takes place in a reactor where retromixing takes place. Furthermore we have shown that the reaction of the invention carried out in a reactor containing two zones can take place in a residence time of the same order as processes carried out in piston reactors.

Finally, reactors containing a portion in which the mixture is homogenised improve heat exchanges and avoid the presence of hot spots in the reactor.

The temperature at which the phosgenation reaction of the invention is carried out is normally from 250°C to 500°C. More particularly, the reaction temperature is from 300°C to 400°C. The term "reaction temperature" means the temperature in the reactor.

The process of the invention can be carried out under pressure, under reduced pressure or at atmospheric pressure. By way of example, the pressure in the reactor can be from 0.5 to 1.5 bars absolute. Preferably, it is carried out at a pressure close to atmospheric pressure.

Once the phosgenation reaction has been completed, the products obtained, as well as the unreacted reactants, are separated using any method which is known to the skilled person.

The isocyanate produced could, for example, be separated by selective condensation in a suitable solvent.

For convenience, the solvent is preferably selected such that its boiling point is greater than the decomposition point of the carbamyl chloride corresponding to the isocyanate formed. In this way, a subsequent step of decomposing the carbamyl chloride is avoided.

Furthermore the solvent must preferably condense at a temperature at which the products, in particular the remaining phosgene and the hydrochloric acid formed, remain in the gaseous state.

The recovered isocyanate is then purified, in particular by distillation.

Regarding the unreacted phosgene, it should be noted that conventional processes recycle this compound to the

reaction step. Because of the very large excesses of phosgene used, these processes are only economically viable if this compound is recycled. However, in this zone of the reaction process there is a large quantity of concentrated phosgene, which may be under pressure, constituting an important problem regarding the safety conditions which must be met.

In a particularly advantageous embodiment of the invention, it is no longer necessary to recycle the phosgene. This eliminates a very important source of problems due to the presence of concentrated phosgene in a particular zone of the process.

In a particular embodiment, the phosgene separated from the reaction products is destroyed using any means known to the skilled person, such as by contact with a base such as caustic soda or with water.

The hydrochloric acid produced can be separated from the reaction products for exploitation (separation of the phosgene present, for example by absorption and distillation) or destroyed by using a base.

It should be noted, however, that recycling the phosgene to the reaction step is perfectly possible and within the scope of the present invention.

In this particular case, the phosgene can be separated from the hydrochloric acid by distillation, absorption in a solvent at a low temperature or any other means, then recycled to the phosgenation process.

The following Examples further illustrate the invention.

EXAMPLE 1

A cylindrical reactor was used, with a diameter equal to its height and a volume of 0.18 l fed by a system of injectors located a quarter of the diameter from the centre of the reactor (separate jets for the amine/solvent mixture and for the phosgene) followed by a 0.12 l tube reactor (30 cm long).

The injection system was of the type described in the article by Matras and Villermaux, Chem Ing Science, 1973, 28, 129.

The following were introduced into the reactor:

- 600 g/h of a gaseous mixture of toluene diamine, 10% by weight, in orthodichlorobenzene, vapourised at 300°C,
- 155 g/h of pure phosgene preheated to 300°C.

The temperature of the reaction mixture in the reactor was 320°C and the average residence time of the reactants was of the order of 3.2 to 3.9 seconds.

After analysis, a yield of more than 95% of toluene diisocyanate was obtained at the outlet to the reactor and no significant clogging was observed in the reactor after more than one hour of operation.

EXAMPLE 2

A cylindrical reactor was used, with a diameter equal to its height and a volume of 0.18 l fed by a system of injectors located a half-diameter from the centre of the reactor (separate jets for the amine/solvent mixture and for the phosgene) followed by a 0.7 l tube reactor (1.4 m long).

The injection system was as described for Example 1.

The following were introduced into the reactor:

- 1100 g/h of a gaseous mixture of toluene diamine, 10% by weight, in orthodichlorobenzene, vapourised at 330°C,
- 196 g/h of pure phosgene preheated to 330°C.

The temperature of the reaction mixture in the reactor was 350°C and the average residence time of the reactants was of the order of 5 to 6.5 seconds.

After analysis, a yield of more than 95% of toluene diisocyanate was obtained at the outlet to the reactor and no significant clogging was observed in the reactor after more than one hour of operation.



CLAIMS

1. A process for the preparation of aromatic compounds substituted by at least two isocyanate groups, wherein at least one compound (A) comprising at least two primary amine functions and at least one aromatic group is brought into contact with an excess of phosgene, the phosgene being in excess by between 0 and 100% with respect to the number of moles of amine functions in compound (A), both reactants being introduced in the gaseous phase, in a mixed reactor comprising a first, homogenising zone corresponding to 20% to 80% of the total volume of the reactor, and a second zone in which the flow is close to piston flow, corresponding to 80% to 20% of the total volume of the reactor.

2. A process according to claim 1 wherein the reaction is carried out in the presence of an excess of phosgene of from 5% to 60% with respect to the number of amine functions in compound (A).

3. A process according to claim 1 or 2, wherein the reaction is carried out in a mixed reactor in which the first zone corresponds to 40% to 80% of the total volume of the reactor and the second zone corresponds to 60% to 20% of the total volume of the reactor.

4. A process according to any one of the preceding claims wherein compound (A) comprises at least one aromatic C₆-C₁₄ group, which is unsubstituted or substituted by one or more linear, cyclic or branched, saturated or unsaturated C₁-C₁₀ hydrocarbon groups.

5. A process according to claim 4 wherein compound (A) comprises at least one aromatic C₆-C₁₀ group.

6. A process according to claim 4 or 5 wherein compound (A) comprises at least one aromatic group substituted by one or more linear, cyclic or branched, saturated or unsaturated C₁-C₁₀ hydrocarbon groups.

7. A process according to claim 6 wherein compound (A) comprises at least one aromatic group substituted by one or more alkyl, aryl, alkyl-aryl or aryl-alkyl C₁-C₁₀ groups.



8. A process according to claim 7 wherein compound (A) comprises at least one aromatic group substituted by one or more alkyl, aryl, alkyl-aryl or aryl-alkyl C₁-C₆ groups.

9. A process according to any one of the preceding claims wherein compound (A) has the formula:



wherein R represents an aromatic group.

10. A process according to claim 9 wherein R represents an aromatic C₆-C₁₄ group which is unsubstituted or substituted by one or more C₁-C₁₀ alkyl groups.

11. A process according to claim 10 wherein R represents an aromatic C₆-C₁₀ group.

12. A process according to claim 10 or 11 wherein R represents an aromatic group substituted by one or more C₁-C₆ alkyl groups.

13. A process according to claim 11 wherein compound (A) is toluene diamine, xylene diamine or phenylene diamine, used alone or as a mixture, with or without their isomers.

14. A process according to any one of the preceding claims wherein at least one of the compound (A) and phosgene is used in the presence of a diluent.

15. A process according to claim 14 wherein the compound(s) (A) are used in a concentration of from 3% to 30% by weight in the diluent.

16. A process according to claim 15 wherein the compound(s) (A) are used in a concentration of from 10% to 20% by weight in the diluent.

17. A process according to any one of the preceding claims wherein the residence time for the reactants in the reactor is from 1.5 to 30 seconds.

18. An aromatic compound substituted by at least two isocyanate groups which has been obtained by a process as defined in any one of the preceding claims.