

1

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POLYMERIZATION OF MONO- AND
POLYMETHYLSTYRENE

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The present invention relates to a method for polymerizing mono- and polymethylstyrenes, and is more particularly concerned with polymerizing said methylstyrenes in a ball mill polymerizer.

The polymerization of methylstyrenes has been hampered by the formation of cross-linked particles, or gels, which foul the equipment and result in loss of product and the time which is required to clean equipment before operations can be resumed.

We have now found that methylstyrenes may be polymerized either batchwise or continuously with essentially no gel formation for indefinite periods of time. Furthermore, if a slight gel formation does occur, it is present in the form of a readily filterable floc which does not plug the equipment and is easily removed from the desired product.

According to our invention mono- and polymethylstyrenes are polymerized by charging said methylstyrenes into a rotating ball mill which is maintained at a polymerizing temperature of from about 90° to about 150° C., and which contains from about 4 to about 12 volume percent, preferably from about 7 to about 9 volume percent of spheroidal objects of at least two different sizes or densities, said densities being between about 4.0 and about 10.0 g./cc. We have further found that the spheroids must be of such size as to form not less than 3 continuous rows across the length of the ball mill, with the larger balls, or balls having a greater density forming at least one row, and that the number of smaller balls, or balls having a lower density, should be not less than $\frac{1}{3}$, and preferably not less than $\frac{1}{2}$ the number of larger balls.

The actual size of the balls will be determined by the size of the ball mill, by the viscosity of the polymerizing mixture in the mill, and by the rotational speed of the mill, but should not exceed 3 to 4 inches in diameter in any case. In operation it is necessary that the smaller or lighter balls be of such weight that they will be carried part way up the wall of the ball mill and then fall back into the mass of larger balls, thus displacing the larger or heavier balls in a transverse direction and preventing the larger or heavier balls from "tracking." When "tracking," that is, following the same path around the drum, they allow gel formation between the respective tracks. This weight will be determined by the rotational speed of the mill and the viscosity of the polymerizing mixture. While it is necessary that at least two different sizes or weights of balls be used the invention is not limited thereto. Three or more sizes or weights of balls may be used to obtain the same results as long as the above mentioned proportions and conditions are met.

We have found that peripheral drum speeds of 50 to 100 feet per minute are satisfactory, with speeds of 64 to 72 feet per minute being preferable. Polymer conversion may be carried to from 10 to 50 percent completion, desirably to from about 35 to about 45 percent. The organic content of the mill should be in the range of 32.0 to 57.0 volume percent for optimum operation. Any temperature from 90° to 150° C. may be used, although temperatures of from 120 to 130° C. are preferred. If it is desired to operate under superatmospheric pressure higher temperatures may be employed.

2

The present invention may be better understood, but is not to be construed as limited by the following examples:

Example I

A ball mill 9 inches long and 6 inches in diameter was rotated at a speed of 41 to 46 r.p.m., i.e. 64 to 72 feet per minute peripheral drum speed, while partially immersed in a constant temperature bath at a temperature of 120° and 125° C. The mill contained 20 stainless steel balls $\frac{1}{2}$ inch in diameter, 22 stainless steel balls $\frac{3}{4}$ inch in diameter, and 22 stainless steel balls 1 inch in diameter. This amounted to 5.3 continuous rows of balls and a total volume of about 7 percent of the volume of the drum. The steel balls had a density of from 7.0 to 8.0 grams per cc. A composition of 95 percent of a mixture of meta- and para-vinyltoluene and 5 weight percent of a mixture of o-, m- and p-diethylbenzene was fed into the mill at a rate of 300 grams per hour through a suitable axial inlet port. Product was removed continuously through an outlet port. Operation was continued for 578 hours and resulted in the formation of only 10 grams of dry filterable floc. There was no build up of gels on surfaces within the polymerizer. The material recovery was 93.8 weight percent having an average polymer content of 41.4 percent.

Example II

A similar run using only a mixture of meta- and para-vinyltoluene as the feed, at a feed rate of 90 to 95 grams per hour and a temperature of 95° C. was carried on for 768 hours with similar results. The average polymer content of the effluent was 27 to 28 weight percent.

Example III

The experiment of Example I was repeated omitting the steel balls entirely and increasing the feed rate to 329 grams per hour to duplicate the residence time. After 775 hours copious quantities of gels had formed on surfaces within the polymerizer necessitating a shut down for cleaning the equipment.

Example IV

Experiments were conducted with less than 3 rows of balls and again the gels began to form and build up. When 10 rows of balls were used (14 volume percent) the mass of balls remained on the bottom with little or no action. Similarly, when only one size of ball was used the balls tended to "track" and form ridges of gels around the walls of the mill.

Similar results are obtained by duplicating the foregoing procedures in a batchwise fashion, i.e. charging the desired monomer into the ball mill which is rotated, while being heated at a selected temperature, until the desired polymerization has occurred, and then removing the organic contents of the ball mill for further processing.

Various modifications may be made in the present invention without departing from the spirit or scope thereof, and it is understood that we limit ourselves only as defined in the appended claims.

We claim:

1. A process for polymerizing ar-mono- and polymethylstyrene which comprises charging said methylstyrenes into a rotating ball mill which is maintained at a polymerizing temperature, and which contains from about 4 to about 12 volume percent, and not less than 3 continuous rows, of spheroids of at least two different weights, with the balls of greater mass forming at least one row and the number of balls of smaller mass being not less than $\frac{1}{3}$ the number of balls of greater mass, and rotating said ball mill at a peripheral speed

3

of 50 to 100 feet per minute thus carrying the balls of smaller mass up the wall of the ball mill to a position from which they fall back into the polymerizing mixture and displace the balls of greater mass to a new position in the continuous row of balls, thereby preventing tracking.

2. The process of claim 1 wherein the polymerization is carried out in a continuous manner.

3. The process of claim 2 wherein the methylstyrene is vinyltoluene.

4. The process of claim 3 wherein the temperature is maintained at from 90° to about 150° C.

5. The process of claim 4 wherein the spheroids are stainless steel balls of at least two different sizes.

4

6. The process of claim 5 wherein about 7 volume percent of the steel balls are employed, forming about 5 rows of said balls in said rotating ball mill.

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