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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO
DIVISIÓN DE NUEVAS CREACIONES

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SUPERINTENDENCIA DE INDUSTRIA Y COMERCIO



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	Trámite	011
	Evento	379
	Actuación	430
	Oficio	5144
	Folios	006

Patente de Invención ☒ Patente de Modelo de Utilidad ☐

Vía Nacional ☐

Vía PCT (fase nacional) ☒ Cap. I ☐ Cap. II ☒

No. solicitud internacional PCT/EP02/11088
Fecha de presentación internacional 2001-11-27

Como resultado del examen de fondo, realizado con fundamento en el artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le comunica:

1. Documentos estudiados

Descripción: folios 152 a 182 (como se modificó mediante oficio de 2008-05-21)
Dibujo: folio 85
Reivindicaciones 1 a 30: folios 183 a 191 (como se modificó mediante oficio de 2008-05-21)
Prioridad: US, 09/724,049 de 00-11-28
Respuesta del solicitante: folios 139 a 149

2. Objeto de la invención

Título de la solicitud: "Polímeros reductores de resistencia y suspensiones y soluciones poliméricas reductoras de resistencia"

El objeto de la presente solicitud de patente de invención consiste en: "Un copolímero de ultra alto peso molecular útil como un reductor de resistencia para hidrocarburos, que comprende: a) un monómero vinil aromático, en donde el monómero vinil aromático comprende uno o más monómeros que se seleccionan del grupo que consiste de estireno, un alquilestireno con un grupo alquilo que tiene entre 1 y 10 átomos de carbono, un vinilnaftaleno y un vinilalquilnaftaleno con un grupo alquilo que tiene entre 1 y 10 átomos de carbono y; b) uno o dos monómeros de α -olefina que tienen una longitud de cadena de

carbono de entre 2 y 20 átomos de carbono; en donde el copolímero de ultra al peso molecular tiene un peso molecular mayor de 5 millones.”

La invención se catalogó como C08F212/02, según la Clasificación Internacional de Patentes (IPC).

3. De la solicitud de Patente

Reivindicaciones (artículo 30 D 486)

El método de la reivindicación 5 prácticamente se ha caracterizado por el resultado a obtener, el cual es un copolímero que comprende un monómero de α -olefina y un monómero vinil-aromático con un peso molecular superior a 1 millón. El afirmar que es un proceso de polimerización en masa no lo hace novedoso porque polimerizar en masa ya era conocido en el estado de la técnica. Así las cosas, no se revela cómo es que realmente se logra el copolímero con el ya mencionado peso molecular, ya que el solicitante afirma en su respuesta que “la persona versada en la materia reconocería que las condiciones exactas a las cuales habría que realizar el proceso de polimerización dependerán del tipo de maquinaria empleada, los monómeros específicos involucrados y la cantidad de estos... por lo tanto no es posible fijar valores exactos para estos parámetros”. El solicitante está prácticamente afirmando que la persona técnica medianamente versada en la materia conoce cómo llevar a cabo el proceso para obtener un copolímero con un peso molecular como el indicado a partir de los monómeros indicados. Por lo tanto, de entrada el propio solicitante está afirmando que el proceso no tiene nivel inventivo. De la misma manera, el proceso de la reivindicación 10 es superfluo porque la persona versada en la materia sabe que en un proceso de polimerización en masa se agrega un iniciador, un catalizador, un promotor. Curiosamente no se menciona nada sobre la manera cómo se logra un peso molecular por encima de un millón, lo cual se debe probablemente al hecho de que esto también era conocido en el estado de la técnica.

Los objetos reivindicados, productos o procesos, no deben caracterizarse por el resultado a lograr (un copolímero de α -olefina y vinilestireno con peso molecular de 1 millón) y por lo tanto la reivindicación 5 y sus dependientes no definen plenamente la materia a proteger.

Las reivindicaciones del copolímero no son coherentes con las reivindicaciones de proceso de preparación del mismo ya que en las primeras se habla de un peso molecular que excede los 5 millones mientras que en las de método el resultado a lograr es solo mayor de 1 millón. En cualquiera de los casos, ese es un resultado a lograr que a juzgar por la respuesta del solicitante ya era alcanzable por un técnico medio en la materia.

Por lo tanto, el capítulo reivindicatorio no cumple con los requisitos establecidos en el artículo 30 de la Decisión 486.

4. Unidad de invención (artículo 25 D 486)

La solicitud carece de unidad de invención porque no hay existe un concepto común inventivo para los objetos de las reivindicaciones 1 a 4, 5 a 9, 10 a 17, 18 a 26 y 27 a 28. Lo común entre estos objetos es un copolímero de α -olefina y vinilestireno que ya era conocido en el estado de la técnica y/o podía derivarse de manera evidente del estado de la técnica por un técnico medianamente versado en la materia. Efectivamente, el copolímero reivindicado ya era conocido en el estado de la técnica en los documentos US 3.700.639, Crystalline polystyrene products (1972-10-24) y no es válido como concepto común a los objetos de las reivindicaciones ya indicadas. Véase el citado documento, tabla III, muestra III-3, donde un copolímero de estireno y α -olefina tiene un peso molecular de 5.200.000.

El uso de dicho copolímero no tiene relevancia según la legislación vigente en Colombia. Por lo tanto, la solicitud no cumple con el requisito de unidad de invención.

5. Determinación del Estado de la Técnica

La fecha tomada en cuenta para determinar el estado de la técnica es 2000-11-28, la cual corresponde a la fecha de prioridad reivindicada.

Debido a que la solicitud carece de unidad de invención, esta oficina no tiene la competencia para seleccionar alguna de las invenciones y efectuarle el examen de patentabilidad. No obstante, es posible afirmar que en el documento US 3.700.639 ya se había divulgado el copolímero reivindicado en la solicitud y por lo tanto no es patentable de acuerdo con lo establecido en el artículo 21 de la decisión 486. Así mismo, tal como están reivindicados los métodos de preparación del copolímero y de su suspensión y solución, es posible afirmar que son los métodos usuales de preparación de cualquier copolímero, de sus suspensiones y soluciones.

Una vez el solicitante adecúe su solicitud de tal manera que cumpla con el requisito de unidad de invención y sea posible identificar una única invención o un grupo de invenciones que conformen un único concepto inventivo, será procedente efectuar el examen de patentabilidad solicitado.

6. Notificación

En cumplimiento del artículo 45 de la Decisión 486 de la Comisión de la Comunidad Andina, se le indica que debe dar respuesta dentro del término de 60 días contados a partir de la fecha de notificación de la presente comunicación. En caso de no dar respuesta al presente requerimiento, o si a pesar de la respuesta subsistieran los impedimentos para la concesión, se denegará la patente.

Notifíquese el presente oficio conforme a lo dispuesto en el numeral 5.2, literal e), del capítulo quinto del título primero de la Circular Única N° 10 de 2001.

ALIX CARMENZA CÉSPEDES DE VERGEL
Jefe de División de Nuevas Creaciones

08 MAYO 2009

El anterior requerimiento fue notificado por fijación en lista, de fecha _____

CONCEPTO TÉCNICO No. 1365	EXAMINADOR TÉCNICO Código No. 202043
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United States Patent Office

3,700,639

Patented Oct. 24, 1972

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3,700,639

CRYSTALLINE POLYSTYRENE PRODUCTS

George E. Hulse and James J. Harris, Pittsburgh, Pa.,

assignors to Sinclair-Koppers Company

Filed Dec. 22, 1971, Ser. No. 210,832

Int. Cl. C08f 15/40, 19/04, 27/26

U.S. Cl. 260—88.2 C

4 Claims

ABSTRACT OF THE DISCLOSURE

Highly crystalline, isotactic polystyrene products having molecular weight of less than 1,000,000 are prepared by the thermal degradation in air at temperatures between 100° C. and 260° C. of high molecular weight, highly crystalline copolymers of styrene with 2–20 percent by weight of an alpha-olefin having 3 to 10 carbon atoms. The initial copolymers have a molecular weight in excess of 1,000,000. The rate of degradation of the copolymers of this invention is greater than the rate of degradation of polystyrene at the same temperatures. The crystallinity of the resulting polystyrene product is generally higher than that of the initial copolymers.

BACKGROUND OF THE INVENTION

This invention relates to a process for the preparation of highly crystalline, isotactic polystyrene products having a molecular weight of less than 1,000,000 which comprises degrading by heating in air of highly crystalline copolymers of styrene having from 2 to 20 percent by weight of an alpha-olefin having from 3 to 10 carbon atoms.

Isotactic polystyrenes prepared by the Ziegler-Natta catalyst system are usually polymers of very high molecular weight (in the millions) and a high degree of crystallinity, and as such are difficult to process by usual molding techniques. To overcome the difficulties of processing, the obvious solution is to degrade the high molecular weight, crystalline polymers to polymers of lower molecular weight (less than 1,000,000). Thermal decomposition in the presence of bromine-containing compounds has been suggested to accomplish the desired degradation. Thermal degradation in the presence of antioxidants has also been proposed.

SUMMARY OF THE INVENTION

It has now been found that highly crystalline polystyrene products of molecular weight between 10,000 and 1,000,000 can be prepared by first preparing highly crystalline, high molecular weight copolymers of styrene containing 2 to 20 percent by weight of an alpha-olefin having from 3 to 10 carbon atoms, and then heating the copolymer in air at a temperature of between 100° C. and 260° C., whereby the copolymer is degraded to polystyrene products having the same or greater degree of crystallinity than the starting copolymers.

These alpha-olefins may be copolymerized with styrene to high molecular weight, crystalline copolymers with the aid of any of the Ziegler-Natta type catalyst systems that are useful for the preparation of isotactic polystyrene.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a graph showing the relative reduction in viscosity versus time of heating at 150° C. of copolymers of styrene containing varying amounts of 1-octene.

FIG. 2 is a graph showing the relative reduction in viscosity versus time of heating at 150° C. of copolymers of styrene containing various alpha-olefins.

DETAILED DESCRIPTION OF THE INVENTION

The copolymers of the invention may be made by copolymerizing styrene with suitable alpha-olefins having

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from 3 to 10 carbon atoms. Suitable alpha-olefins are propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 1-octene, 1-decene, and the like.

The alpha-olefin comonomer should be present to the extent of between 2 and 20 percent by weight of total copolymer. Amounts less than 2 percent gives copolymers whose rate of degradation is not appreciably greater than that of polystyrene. As the amount of comonomers gets greater than 20 percent, the copolymers seem to approach a maximum rate of degradation and the increase in cost of the copolymer offsets any advantage in rate of degradation.

The method of copolymerization is not critical, but the preferred method is to utilize any of the known Ziegler-Natta type catalyst systems whereby highly crystalline, isotactic styrene-alpha-olefin copolymers of high molecular weight are obtained. Thus, a complex catalyst consisting of triisobutyl aluminum with titanium trichloride in heptane at 90° C. gives a polymer of styrene having a molecular weight of about 2,000,000 with a crystallinity of about 26 percent and is suitable for preparing the styrene-alpha-olefin copolymers of the present invention.

The method of heating the copolymers to effect the degradation may be any of several known methods. For example, molding samples of polystyrene containing 4.1 percent propylene in air for 10 minutes at 240° C. followed by annealing at 180° C. for 1 hour causes a drop in molecular weight from 3,000,000 to 470,000. Where the recovery of the sample in the same physical form that one starts with it unimportant, heating may be effected in an extrusion or milling process. Thus, the same styrene-propylene copolymers, after mastication in a Brabender Plasticorder at 200° C. in air had a molecular weight of 105,000 after 15 minutes and of only 72,000 after 30 minutes. A preferred method of heating the copolymers is to place the copolymers in an open dish in a recirculating air oven set at the desired temperature. Temperatures of between 100 and 260° C. may be used, but the preferred temperature range is from 140 to 200° C. Temperatures below 100° C. necessitate an excessively long degradation time, whereas at temperatures above 240° C. (the melting point of isotactic polystyrene), while degradation occurs, the polymeric mass fuses and presents handling difficulties.

The time of heating may be varied from 1 to 24 hours, depending on the final molecular weight desired and the particular copolymer involved. The initial rate of degradation increases with increasing amounts of a particular comonomer in the copolymer as shown in the drawings at FIG. 1. The initial rate of degradation also depends on the particular alpha-olefin which is copolymerized with the styrene as shown by the drawings at FIG. 2, and the Table III. The rate of degradation also increases greatly with temperature of heating as indicated by the data in Tables II and III. The particular time and temperature required to produce a polystyrene of a desired molecular weight can be readily determined by a skilled technician from a knowledge of the composition and molecular weight of the initial copolymer and a few experiments of the type shown in Example II.

The degradation of the crystalline copolymers of the present invention does not cause any loss of crystallinity. In most cases, the crystallinity has been increased by the heating process. It is not known whether the increase in crystallinity is due solely to annealing effects or to the molecular weight breakdown giving smaller molecules which are better able to crystallize. For example, a styrene-propylene copolymer having 5.0 percent propylene, initial molecular weight of 2,000,000 and an initial crystallinity of 26.25 percent was degraded by heating in air for 6 hours at 200° C. to form a polystyrene product of

molecular weight of 24,000 and a final crystallinity of 39.5 percent. Similarly, a copolymer of styrene with 5.7 percent 1-octene having an initial molecular weight of 4,500,000 and a crystallinity of 18.3 percent was degraded for 24 hours at 150° C. to give a product of molecular weight 290,000 and a crystallinity of 34.1 percent. All crystallinities were measured by differential scanning calorimetry.

Molecular weights of the various polystyrene products were calculated from the intrinsic viscosity in chlorobenzene at 30° C. on the basis of the formula

$$[\eta] = KM^a$$

where

$[\eta]$ = intrinsic viscosity in 100 cc./g.

$K = 1.8 \times 10^{-4}$

$a = 0.72$

M = viscosity average molecular weight.

The same formula was used to calculate the molecular weights of the styrene-alpha-olefin copolymers, although admittedly this is an approximation.

The following examples are given to illustrate the invention.

Example I

The general procedure used to prepare the copolymers of this invention was as follows:

A two-liter resin pot was equipped with a turbine stirrer, a thermometer, a dropping funnel, and a charging port containing a self-sealing rubber stopper through which catalyst could be added by means of a syringe. The apparatus was baked at about 150° for 18 hours while nitrogen was passed through the pot. After the apparatus was thus conditioned, it was cooled under nitrogen and the desired amounts of titanium trichloride catalyst were added through the charging port. Next, a measured amount of triisobutyl aluminum cocatalyst was added by syringe through the charging port. The heptane solvent was then added through the dropping funnel. The styrene and comonomer were then mixed and added to the drop-

particles when the stirrer was stopped. The copolymers were recovered by filtration, washed with methanol and dried.

To illustrate the method, a series of copolymerizations were run using styrene and 1-octene mixtures of varying ratios. The amounts of catalyst, solvent, and monomers are given in Table I along with the percent yield of copolymers, the copolymer composition, the intrinsic viscosity of the copolymers, and the percent crystallinity of the copolymers.

TABLE I
Copolymerization of Styrene with 1-Octene

Run No.	I-1	I-2	I-3	I-4	I-5	I-6	I-7
TiCl ₃ , g.	0.89	1.00	0.81	0.94	1.07	1.00	1.05
Iso-Bu ₃ Al, ml.	2.27	2.55	2.05	2.40	2.70	2.55	2.65
Heptane, ml.	289	550	643	582	521	700	1090
Styrene, ml.	445	490	385	423	482	400	267
1-octene, ml.	0	10	20	47	53	100	157
Yield, percent	29.0	38.2	42.6	43.1	47.4	47.7	42.7
Intrinsic viscosity, $[\eta]$	4.15	6.90	8.12	7.93	6.74	6.45	4.61
Octene in copolymer, mole-percent	0	2.1	3.3	5.7	9.0	15	31
Crystallinity, percent	25	10.2	25.1	18.3	12.9	17.7	10.9

^a Intrinsic viscosity measured in chlorobenzene at 30° C.

^b Copolymer analysis by nuclear magnetic resonance.

^c Crystallinity determined by differential scanning calorimetry.

It can be seen from the Table I that copolymers containing from 2.1 to 31 mole percent of 1-octene have been prepared by varying the amounts of monomers, catalyst, and solvent used. The crystallinities of the resulting copolymers may be increased by annealing the samples.

Example II

To illustrate the increased rate of molecular weight degradation of the styrene/1-octene copolymers over the rate of degradation of the polystyrene, the polymer and copolymers prepared in Example I were heated in the presence of air at the temperatures shown and for the times indicated in Table II. The degradation in molecular weight, and the drop in intrinsic viscosity of the samples, is shown in the Table II and the initial rate of degradation is shown graphically in FIG. I of the drawings.

TABLE II
Degradation of Styrene/1-Octene Copolymers

Sample No.	Mole percent 1-octene	Initial molecular weight ^a		Molecular weight ^b after degradation				$[\eta]_0/[\eta]$
		$[\eta]_0$	Mv	Hours	Temp., ° C.	$[\eta]$	Mv	
I-1	0	4.15	1,900,000	6	150	5.00	2,400,000	1.21
				24	150	4.42	2,100,000	1.06
I-2	2.1	6.90	3,800,000	6	150	4.83	2,800,000	0.70
				24	150	3.13	1,800,000	0.46
				6	180	2.41	900,000	0.35
				24	180	0.51	105,000	0.074
I-3	3.3	8.12	4,700,000	6	150	5.19	2,600,000	0.64
				24	150	2.55	980,000	0.31
				6	180	2.26	820,000	0.23
				24	180	0.495	100,000	0.061
I-4	5.7	7.93	4,500,000	6	150	3.72	1,650,000	0.47
				24	150	1.05	290,000	0.13
I-5	9.0	6.74	3,600,000	2	150	4.75	2,250,000	0.71
				4	150	2.46	920,000	0.37
				6	150	1.28	350,000	0.19
I-6	15.0	6.45	3,400,000	2	150	1.63	530,000	0.25
I-7	31.0	4.61	2,200,000	2	150	0.46	91,000	0.10

^a $[\eta]_0$ = Initial intrinsic viscosity measured in chlorobenzene at 30° C. Mv = viscosity average molecular weight calculated from $[\eta]_0$.

^b $[\eta]$ = Intrinsic viscosity after degradation measured in chlorobenzene at 30° C. Mv = viscosity average molecular weight calculated from $[\eta]$.

ping funnel. All manipulations were performed under a head of nitrogen. The stirrer was then started and allowed to stir at about 1,000 r.p.m. throughout the polymerization. When the resin pot had been heated to 90° C., the monomers were added dropwise from the funnel, while controlling the temperature of the reaction mixture at 90° C. $\pm$ 2° C. After about 6 hours, the reaction mass was allowed to cool to about 60° C. and the catalyst was killed by the addition of 200 ml. of methanol followed by stirring and heating to reflux for one hour. The copolymers settled out to the bottom of the pot as white

Referring to FIG. I of the drawings, the viscosity of the copolymer after degradation has been divided by the initial viscosity in order to normalize all the curves to a single starting point. It may be seen from the figure that the initial rate of degradation in molecular weight increases as the mole percent of 1-octene in the copolymer increases. The increase in viscosity of the polystyrene sample I-1 is probably due to a small amount of cross-linking which occurs prior to degradation. The sample then starts to degrade as indicated by the 24 hour heating.

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Example III

To illustrate the general applicability of the use of alpha-olefins as an aid to more rapid degradation of molecular weight of crystalline polystyrene, a series of copolymers was made by the general method outlined in Example I. The mole percent comonomer in the copolymers and the initial intrinsic viscosity of the copolymers is recorded in Table III. Each copolymer was subjected to heat in the presence of air from 1 to 24 hours and the resulting intrinsic viscosity measured. The results are also tabulated in Table III. Molecular weights are included for convenience.

TABLE III
Degradation of Styrene/alpha-Olefin Copolymers

Sample No.	Comonomer, mole and in copolymer	Initial molecular weight ^a		Molecular weight ^b after degradation				[η]/[η] ₀
		[η] ₀	Mv	Hours	Temp., ° C.	[η]	Mv	
III-1.....	None, 0.....	4.15	1,900,000	6	150	5.0	2,400,000	1.21
				24	150	4.42	2,100,000	1.06
III-2.....	Propylene, 5.0.....	4.37	2,000,000	6	150	2.87	1,150,000	0.66
				24	150	0.79	190,000	0.18
				6	200	0.18	24,000	0.041
				24	200	0.08	7,800	0.018
III-3.....	3-methyl-1-butene, 20..	8.65	5,200,000	6	150	6.19	3,250,000	0.72
				24	150	3.64	1,600,000	0.42
				6	200	0.28	45,000	0.032
				24	200	0.16	20,500	0.018
III-4.....	1-pentene, 16.0.....	8.59	5,000,000	4	150	2.21	800,000	0.28
				6	150	1.87	640,000	0.22
III-5.....	1-pentene, 20.0.....	7.40	4,200,000	2	150	4.50	2,100,000	0.61
				6	160	3.62	1,500,000	0.48
III-6.....	1-pentene, 35.0.....	6.82	3,700,000	1	150	4.39	2,000,000	0.64
				3	160	0.77	190,000	0.11
III-7.....	1-hexene, 7.0.....	5.1	2,500,000	6	150	4.25	1,950,000	0.83
				24	150	3.94	1,750,000	0.77
				6	180	0.61	135,000	0.12
				24	180	0.25	38,500	0.049
III-8.....	1-hexene, 12.0.....	4.78	2,300,000	6	150	1.85	620,000	0.39
				24	150	0.92	240,000	0.19
III-9.....	1-hexene, 22.0.....	5.59	2,800,000	6	150	0.77	190,000	0.14
				24	150	0.36	65,000	0.064
III-10.....	1-decene, 6.0.....	7.47	4,200,000	4	150	4.99	2,400,000	0.67

^a [η]₀=Initial intrinsic viscosity determined in chlorobenzene at 30° C. Mv=viscosity average molecular weight calculated from [η]₀.
^b [η]=Intrinsic viscosity after degradation measured in chlorobenzene at 30° C. Mv=viscosity average molecular weight calculated from [η].

From the table it is apparent that the use of 180° C. or 200° C. rather than 150° C. for the degradation greatly increases the rate of molecular weight decrease. FIG. 2 of the drawings is a normalized plot of relative initial rates of degradation at 150° C. There is no apparent correlation between number of carbons of the alpha-olefin and the rate of degradation of molecular weight.

What is claimed is:

1. A process for preparing a highly crystalline, isotactic polystyrene product having a molecular weight of less than 1,000,000 comprising:

(a) preparing a highly crystalline, isotactic copolymer having a molecular weight of greater than 1,000,000 and consisting of styrene and from 2 to 20 percent by weight of an alpha-olefin having from 3 to 10 carbon atoms; and

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(b) lowering the molecular weight of said copolymers by heating it in air at a temperature of between 100° C. and 260° C. until the desired molecular weight has been obtained, whereby the rate of degradation is increased over the rate of degradation of crystalline polystyrene while the degree of crystallinity of the resulting product is increased over that of said copolymer.

2. The process of claim 1 wherein said alpha-olefin is selected from the group consisting of propylene, 1-butene, 1-pentene, 3-methyl-1-butene, 1-hexene, 1-octene, and 1-decene.

3. The process of claim 1 wherein said heating is carried out at a temperature of between 140° C. and 200° C.
4. The process of claim 1 wherein said lowering of the molecular weight of said copolymer comprises heating by milling in air at a temperature of between 100° C. and 260° C.

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JAMES A. SEIDLECK, Primary Examiner

R. S. BENJAMIN, Assistant Examiner

U.S. Cl. X.R.

260-88.2 S