CHLORINATION OF POLY(VINYL CHLORIDE) IN LIQUID CHLORINE, AND CHLORINATED POLY(VINYL CHLORIDE) COMPOSITION.

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The file contains technical information submitted after the application was filed and
not included in this specification

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Description

Background of the invention

The excellent heat distortion temperature of chlorinated poly(vinyl chloride) resins (hereinafter "CPVC" for brevity) predates their use in applications where poly(vinyl chloride) resins (hereinafter "PVC" for brevity) would otherwise be chosen. CPVC resins are derived by chlorination of PVC, a reaction which has been studied in great detail over the past twenty years or so, during which numerous chlorination processes have been developed. More preferred is a process carried out by suspending PVC in water, which PVC is swollen with a halogenated lower hydrocarbon swelling agent, and irradiating swollen PVC with ultraviolet light (actinic radiation) while bubbling chlorine gas ("Cl₂") into the water. This process is disclosed in U.S. Patent No. 2,996,489 to Dannis, M. L. and Ramp, F. L. Several subsequent inventions related to this basic process have been disclosed in the textbooks “Polyvinylchlorid und Vinilchlorid-Mischpolymerisate”, pp 120–125, Springer, Berlin (1951); “Vinyl and Related Polymers,” by C. A. Schlicknecht (1952); and in U.S. Patents Nos. 2,426,808; 2,890,651; 3,100,762; 3,334,077; 3,334,078; inter alia. The disadvantage of these liquid-phase processes in which the reaction occurs in an aqueous medium, is that (a) chlorine dissolves in water with difficulty, and even at elevated temperature and pressure, chlorinated product forms relatively slowly; and, (b) it is only with difficulty and expense that essentially all the swelling agent used in these processes can be removed from the CPVC product.

Other chlorination processes use reaction in an inert liquid medium (which liquid does not react with PVC), without a swelling agent, such as those disclosed in German patent No. 2,322,884 published Nov. 22, 1973; U.S. Patents Nos. 3,506,637 and 3,534,013; inter alia. Still other less preferred chlorination processes using an inert liquid medium comprise dissolving or suspending the resin in a chlorinated hydrocarbon solvent and promoting the reaction with heat, light, or a catalyst. Yet other processes utilize a fluidized bed of PVC which is contacted with Cl₂ gas, optionally diluted with an inert gas, and optionally also containing a lower chlorinated hydrocarbon, again catalyzed by ultraviolet radiation. Such processes have been disclosed in U.S. Patents Nos. 3,532,612; 3,663,392; 3,813,370; Japanese Patent No. 49-45310; British Patent Specifications 1,089,323; 1,242,158; 1,318,078; and, German Patents Nos. 1,110,873; 1,259,573; inter alia. These fluidized bed chlorination processes occur in a gaseous reaction medium, but with difficulty, because of the slow gaseous diffusion of Cl₂ into solid PVC macrogranules. The term “macrogranules” is used herein to define a cluster or aggregate of randomly closely packed primary particles of suspension PVC. A handful of macrogranules has the feel of fine sand, and are also referred to as "grains". A macrogranule of suspension PVC or CPVC will typically have an average diameter of from about 100 to about 150 μm. A preferred size distribution of each macrogranule is in the range from about 50 to about 500 μm, and conventionally ranges from about 100 to about 200 μm. Each macrogranule is made up of a multiplicity of primary particles each in the size range from about 0.05 μm to about 5 μm, and more typically in the range from about 0.5 μm (5000A) to about 2 μm (20,000A). The bulk of the primary particles are usually submicronic in size, though conditions of polymerization will determine the actual size distribution of both primary particles, and also macrogranules. Macrogranules can be characterized by their porosity, that is, internal pore volume, and surface area.

The morphology of PVC and CPVC macrogranules, specifically the porosity and surface area, are important properties which determine the physical properties of an article after the polymer is molded. Since CPVC is generally derived by the chlorination of PVC, it has been found that the properties of product CPVC may be tailored to a large extent by precisely controlling the conditions under which precursor PVC is polymerized. Such a process is disclosed in U.S. Patents Nos. 3,506,637 and 3,534,103. With care, the internal morphology of PVC macrogranules may be particularly tailored to permit relatively fast chlorination in a fluidized bed process catalyzed by actinic radiation. Even so, it is necessary for economy, to practice the process in two stages, as disclosed in U.S. Patent No. 4,038,732 to Stamicarbon B.V.

I am aware that it is known to chlorinate solid crystalline polyethylene ("PE") by reacting between 5 to 100 parts of liquid Cl₂ per part of PE, in a reaction medium of liquid Cl₂ until the resulting chlorinated PE (hereinafter “CPE” for brevity) dissolves in the liquid Cl₂ and then to recover CPE by evaporating the Cl₂. This process is described in greater detail in Canadian Patent No. 471,037 to John L. Ludlow which teaches a process for the chlorination of ethylene polymers. In this process, PE is suspended in at least 5 parts liquid Cl₂ and irradiated with a suitable light source. As taught by Ludlow, the chlorination of PE which is crystalline and has no chlorine bound in its structure, proceeds from the surface inwardly, the chlorinated polymer dissolving in the chlorine substantially immediately upon its formation, thereby exposing unchlorinated polymer. The PE is not homogeneously chlorinated.

A similar orthochlorination of polymers is known from Chemical Abstracts Vol. 83, page 22, number 164 879h: chlorinated polymers were post-chlorinated by dissolving in a liquid chlorine at −30 to 100°C in the presence or absence of UV or radioactive rays. Obviously this teaching refers to polymers other than PVC which does not dissolve in liquid chlorine.

Quite surprisingly, however, the chlorination of PVC in liquid Cl₂ results in the substantially homogeneous chlorination of the PVC. By
Homogeneity of CPVC having Cl content of at least 65% by wt uniquely characterizes the CPVC produced by the process of this invention. This homogeneity is attributed to the presence of Cl throughout the PVC polymer. The presence of Cl on the backbone allows the PVC to swell in liquid Cl₂ sufficiently to form a gel phase which allows rapid reaction. In other words, CPVC contains a gel phase in the PVC, swelling it without producing a solution of PVC in Cl₂. Thus, CPVC produced in my invention is a G-product quite distinct from CPVC resins prepared in solution (“solution chlorinated”) and referred to as L-product (see “Encyclopedia of PVC” edited by Leonard L. Ness, Chapter 6 “Chemically Modified Polyvinyl Chloride”, p. 229). PE is not chlorinated by a gel type chlorination. Though PE and PVC may each be chlorinated in liquid chlorine, many polymers of monofunctionally unsaturated monomers are not chlorinated in liquid Cl₂ or only slightly chlorinated. For example, poly(vinyl fluoride), and poly(vinylidene chloride-vinyl chloride, 88:12) are not chlorinated; and, as Ludlow taught, unless PE is suspended in at least 5 parts by weight liquid Cl₂, there is very little chlorination.

In my U.S. patent application Serial No. 177,969 filed August 14, 1980, there is disclosed a process for the relatively dry chlorination of PVC macrogranules in which only sufficient liquid Cl₂ is used as will “wet” the macrogranules without any visual appearance of having been “wetted”. The terms “wet” and “wetted” are used herein to refer solely to the presence of liquid Cl₂ on macrogranules of polymer, and not to the presence of water. When the requisite amount of liquid Cl₂ within a narrowly specified range is absorbed by the solid PVC which is then irradiated with actinic (ultraviolet) radiation, there results a reaction in the solid PVC medium which produces a CPVC product which is distinguishable over prior art CPVC products formed by prior art methods. In this “relatively dry chlorination of PVC” the reaction proceeds in a solid medium, the liquid Cl₂ having diffused into the solid PVC without affecting its free-flowing nature.

I am unaware of any process for the chlorination of PVC macrogranules by a reaction which occurs in a gel phase in a suspension of PVC in liquid Cl₂. It is the peculiar characteristic of such a reaction which results in the substantially homogeneous chlorination of the PVC. It is reported to be possible to obtain “uniform chlorination” of PVC in water (see Takadono, Yoshido and Fukawa in Kogyo Kagaku Zasshi, Vol 67, No. 11, 1928 (1964); C.A. 62, 13262h), but this requires the assumption that Cl₂ is a solvent for PVC and the Cl₂ will thus enter even the most crystalline regions (see “Encyclopedia of PVC” supra, p 228). A homogeneously chlorinated PVC prepared in a suspension of PVC in hydrochloric acid is also reported by Seidel, Singer and Springer in Ger.(East) Pat. No. 32586; (C.A. 63, 7130f). In each case, the light-catalyzed reaction was of extremely long duration, about 8 hours. Since my reaction proceeds very rapidly despite being a gel type chlorination, it is clearly a distinctly different process.

It should also be noted that in U.S. Patent No. 2,996,488 it is stated that the CPVC made therein has “a structure in which at least 75%, more preferably at least 95%, and most preferably essentially all (i.e. 97—98%) of the chlorinated vinyl chloride units at 1,2-dichloroethane units. Such products are thus distinguished over prior art CPVC resins which contain a significantly higher proportion (i.e. greater than 10%) of the chlorinated vinyl chloride units as the undesirable 1,1-dichloroethylene units” (see top of col 2). This statement was based on chemical analysis of the CPVC prepared by using chloroform and other hydrochloromethylene compounds as swelling agents in the US—A—2 996 488 process. At that time, pulsed Fourier transform ¹³C nuclear magnetic resonance (“Nmr” for brevity) spectra were not available, and the details of the structure of CPVC revealed through analysis of the spectra were not known. The Nmr spectra presented herewith provide an insight into the structure of prior art materials as well as those prepared by the high liquid chlorination process of this invention. Comparison of these spectra graphically highlights their similarities and differences. Analysis of the spectra are based on studies such as those described in “Determination of Tetrad Concentration in Poly(vinyl chloride) Using Carbon-13 Nuclear Magnetic Resonance Spectroscopy” by Carman, Charles J., in “Macromolecules”, Vol 6, pg 725 et seq, Sept-Oct 1973.

It has been discovered that solid, discrete, macrogranules of poly(vinyl chloride), “PVC” for brevity, when slurried in at least 5 times their weight of liquid chlorine (“Cl₂”), absorb the liquid so as to swell the PVC sufficiently to produce a gel phase which allows the PVC to be homogeneously chlorinated. Upon chlorination of the slurry in the presence of actinic (ultraviolet) radiation, a gel-type reaction occurs in the gel phase, within and around swollen macrogranules. This reaction occurs at a temperature in the range from about −50°C to about 50°C and a...
pressure sufficient to maintain the Cl₂ in the liquid phase, and unexpectedly produces the homogeneously chlorinated 'chlorinated poly(vinyl chloride)', 'CPVC' for brevity, having a Cl content of at least 65% by wt, in which the mol ratio of PVC present in a sequence of 3 or more vinyl chloride ('VC') units, to the mol of total VC units, is always less than 0.30.

It has also been discovered that because of the swelling of the PVC which produces a gel phase prior to commencement of the chlorination reaction in the presence of ultraviolet light, the sites of the replaceable hydrogen atoms in both the amorphous and crystalline regions of the PVC are essentially randomly chlorinated to yield a novel CPVC composition. Unexpectedly, the product CPVC formed by this “high liquid chlorine” process is readily distinguishable over prior art CPVC compositions, particularly by ¹³C nuclear magnetic resonance (“Cnmr”) analysis. In this homogeneously chlorinated composition, the tacticity ratio in the CPVC is substantially the same as the tacticity ratio of the PVC from which it was derived. A comparison of thermal data for the novel CPVC composition with thermal data for prior art CPVC compositions, each with the same Cl content, also distinctly distinguishes the one from others.

It is therefore, the object of this invention to provide a process for the chlorination of solid porous macrogranules of PVC, having a Cl content in the range from about 55 to about 57% by wt, suspended in an excess of liquid Cl₂, to produce a homogeneously chlorinated CPVC product with a Cl content of at least 65%. Since chlorine provides the dual function of reactant and swelling agent, the use of conventional swelling agents, or other reaction aids whether catalytic or not, is avoided. Also avoided is the difficult problem of removing such aids from the CPVC product.

It has also been discovered that the “high liquid chlorine” gel-phase chlorination process of this invention is readily adaptable to a continuous process in which macrogranules of PVC are slurried in at least 5 times their weight of liquid Cl₂ near one end of a reaction zone maintained at a temperature in the range of from −50°C to about 50°C, for a period of time sufficient to cause their swelling, and agitating in the reaction zone while being exposed to actinic radiation. After a period of time sufficient to convert the PVC into CPVC containing a predetermined amount of chemically-bound Cl in the CPVC, a solution of homogeneously chlorinated CPVC in liquid Cl₂ may be continuously recovered from near the other end of the reaction zone. The amount of Cl in the range from 65% to about 73% by wt, which replaces replaceable H atoms in the PVC may be controlled by adjusting the process conditions under which the chlorination takes place, but cannot be exceeded by the process of this invention. By-product hydrogen chloride (HCl) gas formed during the reaction is removed from the reaction zone; and concurrently evolved Cl₂ gas is optionally condensed and recycled as liquid Cl₂ to the reaction zone.

It is therefore a general object of this invention to provide a process for the continuous photochlorination of a mass of PVC macrogranules slurried in from about 5 to about 50 times their weight of liquid Cl₂ for a sufficient period of time prior to photochlorination, so as to allow absorption of the Cl₂ into the macrogranules, and their swelling to provide a gel phase within and around each macrogranule. Upon chlorination in the presence of ultraviolet radiation some or all of the Cl₂ evolved during reaction, may be returned to the reaction zone as liquid.

Yet another discovery is that the CPVC formed may be recovered from its solution in liquid Cl₂ by adding to the solution a solvent for Cl₂ in which solvent CPVC is essentially insoluble, so as to form a three-component mixture, and then recovering solid CPVC from the three-component mixture.

It is therefore a specific object of this invention to provide a simple and effective process for recovering solid porous CPVC from a mixture of CPVC dissolved in Cl₂ by adding a halogenated lower alkane (“HLA”) to dissolve the Cl₂ to form a three-component mixture from which CPVC may be recovered as a solid phase.

Brief description of the drawings

The invention will be more readily understood from the following detailed description of the process and the composition produced from it, taken in conjunction with schematic illustrations of the process, Cnmr spectra and photomicrographs of the PVC starting material and chlorinated products derived from them, set forth in the accompanying drawings, wherein:

Figure 1 is a flowchart schematically illustrating the principal features of a batch process for the chlorination of a wet slurry of PVC macrogranules slurried in at least 5 times their weight of liquid chlorine.

Figure 2 is a flowchart which schematically illustrates the principal features of a continuous process for the “high liquid chlorination” of PVC macrogranules in a slurry having a large excess of liquid chlorine.

Figure 3 is a trace of a Cnmr spectra of a Geon® 103EP PVC having a Cl content of about 56.7% by wt such as is typically obtained by suspension polymerization of vinyl chloride.

Figure 4 is a Cnmr spectra of CPVC obtained by suspension chlorination in water of PVC having a Cl content of 56.7%. The Cl content of the CPVC is 71.2% by wt.

Figure 5 is a Cnmr spectra of CPVC obtained by the high liquid chlorination process of this invention. The Cl content of the CPVC is 69.8% by wt. The PVC starting material is the same as that used in the aqueous suspension chlorination of PVC.

Figure 6 is a Cnmr spectra of CPVC obtained by solution chlorination of the aforementioned PVC.
The Cl content of the solution chlorinated CPVC is 68.3% by wt.

Figure 7 is a photomicrograph, at 20× magnification, of a typical mass of discrete macrogranules of Geon 110×352 PVC.

Figure 8 is a photomicrograph, at 20× magnification, of chlorinated Geon 110×352 PVC after it has been soaked in liquid Cl₂ so as to swell and form a gel phase, after which the Cl₂ is removed.

Figure 9 is a photograph, at 30× magnification, of Geon 103EP PVC resin.

Figure 10 is a photograph, at 30× magnification, of Geon 603×560 CPVC resin obtained by chlorination of an aqueous suspension of 103EP PVC shown in Fig. 9.

Figure 11 is a photograph, at 30× magnification, of homogeneously chlorinated CPVC resin made by chlorination in liquid Cl₂ and recovered by precipitation of the solid from its solution in liquid Cl₂ by the addition of a solvent for Cl₂, showing the characteristic non-spherical powdery form of CPVC obtained.

Detailed description of the invention

The high liquid chlorination process of this invention is not only unexpectedly efficient, but it also produces, directly, a CPVC composition which is distinguishable from prior art compositions. The efficiency of this process is attributable to the high concentration of Cl₂ molecules and their swelling effect on PVC particles which produces a gel phase and permits Cl addition to both amorphous and crystalline regions of the PVC with equal probability so that a homogeneously chlorinated polymer is obtained having (i) a chlorine content greater than 65 percent by weight,

(ii) a determinable glass transition temperature,

(iii) in a 13C nuclear magnetic resonance spectrum of said CPVC, a first peak at about 41 ppm said first peak being greater than other peaks in the range from about 37 to about 45 ppm, and

(iv) a second peak at about 63 ppm, said second peak being greater than other peaks in the range from about 57 to 70 ppm.

The chlorine content is preferably at least 70 percent by weight, and, said spectrum has no detectable syndiotactic-peak in the range from about 45 to 50 ppm. Though PVC is known to be photochlorinated in a gel phase produced by swelling the PVC with certain chlorohydrocarbons, it was not expected that a photochlorinatable gel phase would be obtained when PVC is suspended in liquid Cl₂, nor that such a gel phase in liquid Cl₂ would yield homogeneously chlorinated CPVC.

Figs. 7 and 8 are photographs, each at 20× magnification, of a typical commercial PVC homopolymer such as Geon® 110×352 before (Fig. 7) and after (Fig. 8) it is soaked in liquid chlorine and then dried. In Fig. 7, all macrogranules have a milk-white appearance. In Fig. 8 the arrows point to some of the macrogranules which have a distinctive translucent appearance due to the formation of a gel phase. All macrogranules in Fig. 8 are generally the same size as the original PVC macrogranules in Fig. 7 because, upon drying after soaking, they have reverted to their original size because the liquid Cl₂ is removed. As long as the macrogranules contain liquid Cl₂ they are swollen. Other macrogranules which appear milk-white in Fig. 8 also include a gel phase which is formed in varying degrees of completeness not sufficient to be seen in this photograph.

In the process of this invention, the PVC starting material must have three essential characteristics, namely (1) a high molecular weight; (2) a macrogranular form; and (3) adequate purity and freedom from contamination and degradation. These and other characteristics of the PVC starting material are disclosed in greater detail in U.S. Patent No. 3,986,485.

The process of this invention is peculiarly adapted to the photochlorination of vinyl chloride homopolymer having a Cl content in the range from about 55% to about 57% by wt despite its crystallinity, and also because of the peculiar particle morphology of these PVC macrogranules. In the most preferred embodiment of this invention, the process is used for chlorinating solid macrogranules of homopolymers of vinyl chloride, prepared by emulsion, suspension, solution or bulk polymerization techniques to yield a polymer having a relatively high molecular weight in the range from about 100,000 to about 1,000,000. Most preferred are porous macrogranules of PVC produced in an aqueous suspension. The molecular weight of PVC may be related to its specific viscosity which is determined in a known manner. The PVC starting material in the process of this invention has a high molecular weight such that it possesses a specific viscosity of at least 0.20.

The photochlorination process of this invention is carried out at a temperature below the condensation point of Cl₂ as it is critical that the Cl₂ absorbed within the macrogranules of PVC be present in the liquid state, under the pressure conditions of the reaction. It is more preferred that the temperature of reaction be substantially below the condensation point of Cl₂ at the pressure at which the reaction is to be carried out. This preferred temperature of reaction is in the range from about -50°C to about 50°C, though a temperature as high as 70°C is operable. At atmospheric pressure this temperature of reaction is preferably in the range from about -50°C to about -40°C, though lower temperatures as low as about -80°C may be employed. At 6.895×10⁸ Pa (100 psig), the reaction temperature is about 25°C, and even higher pressures and correspondingly higher temperatures may be used. However, above about 6.895×10⁹ Pa (100 psig) the benefits due to better diffusivity of liquid Cl₂ into the macrogranules of PVC begin to be vitiated by the economic penalties of operating at the higher pressures.

*Geon is a Registered Trademark of the B.F. Goodrich Company.
Liquid chlorine is absorbed into macrogranules of PVC by pumping the liquid into a mass of granules which is being mildly agitated so as to present fresh macrogranule surfaces to the liquid which is quickly absorbed into the macrogranules thus coming into contact with the primary particles which constitute a macrogranule. By the term "absorbed" I refer to liquid chlorine held within a macrogranule, irrespective of whether the precise mechanism of holding the chlorine entails absorption, adsorption, chemisorption or physisorption. The amount of liquid chlorine pumped on to the mass of PVC to be chlorinated is in the range from about 5 parts by about 50 parts by weight chlorine per part by weight of PVC. In this range, and in the more preferred range of from about 5 to about 30 parts by weight liquid Cl₂ per part by weight of PVC, the mass appears to be a freely pumpable liquid slurry. Calculations indicate that 1.13 parts by weight liquid Cl₂ per part of PVC is sufficient to yield, theoretically, a CPVC with a chemically bound Cl content of 73.1%; but, unless a large excess of Cl₂ at least 5 times as much by weight as the amount of PVC is used, the PVC will not be homogeneously chlorinated. The precise amount of Cl₂ actually introduced into the polymer after the chlorination reaction is completed will further depend upon the time of the reaction, the intensity of the ultraviolet radiation, and the physical and chemical characteristics of the PVC starting material. It will be evident that the physical and chemical characteristics of the CPVC product will vary according to the process condition under which it was formed, and that a particular CPVC product may be obtained by routine and simple trial and error to stabilize all the variables.

Since liquid Cl₂ itself is the critical swelling agent, no additional swelling agents are either necessary or desirable in the process of this invention, so that upon photochlorination, only hydrogen chloride (HCl) trapped in the macrogranules, and liquid Cl₂ not consumed in the reaction are to be removed. Because the chlorination reaction is exothermic, the temperature of the reaction mass will tend to rise. Some Cl₂ may be evolved along by product HCl, and evaporation of the Cl₂ tends to allow the reaction to proceed substantially isothermally. In general, additional cooling may be required to maintain the desired temperature of the mass of PVC macrogranules, and condensed Cl₂ so conveniently removed as gas, and Cl₂ may be condensed and recycled to the reaction, if desired, as is explained in greater detail hereinbelow.

Any form of actinic radiation is suitable; for example, ordinary incandescent lamps, mercury vapor or arc lamps, neon glow tubes, fluorescent tubes, carbon arcs and sodium vapor lamps may be employed. Ultra-violet light is the preferred source of illumination. In order to obtain a highly heat-stable chlorinated resin when the chlorination is stimulated by photolllumination, the intensity of illumination is desirably controlled to avoid surges in temperature.

The CPVC product formed by the high liquid Cl₂ process of this invention is distinguishable from prior art CPVC not only by its spectral "finger-print", but also by its physical characteristics, particularly its appearance. A visual examination of the CPVC product under 20× magnification shows that the majority of particles appear milky white but, irrespective of how the CPVC is recovered from its solution in liquid Cl₂, quite dissimilar to the PVC macrogranules from which the CPVC was derived. A more detailed comparison shows the difference in internal structure, and in particular, for CPVC recovered with a HLA solvent for chlorine, a distinctly different particle morphology.

Fig. 9 is a photogprah, at 30× magnification of a sample of commercial CPVC. Fig. 10 is a photograph, also at 30× magnification, of a sample of commercial Geoxx 603×560 CPVC resin which is made by the chlorination of an aqueous suspension of the 103EP resin. Fig. 11 is a photograph, also at 30× magnification, of a sample of powderly homogeneously chlorinated CPVC recovered by precipitation with an HLA according to the process of this invention. It is seen that the particles of the powderly CPVC do not have the typical generally spherical form of the macrogranules shown in Figs. 9 and 10, but are of non-uniform shape, and most of the particles are agglomerated. Even as agglomerates the particles in Fig. 11 have a distinctly translucent appearance quite different from the appearance of the macrogranules of CPVC in Fig. 10. Other morphological differences are not apparent in these photographs.

The surface area and other physical properties of the CPVC obtained will depend upon the conditions of chlorination, the particular characteristics of the starting PVC resin, the Cl content of the CPVC, the method by which the CPVC is recovered from its solution in Cl₂ and other factors. Surface area is measured by the BET method using the nitrogen adsorption, as more fully described by Brunauer, Emmett and Teller in J.A.C.S. 60, 309–319, (1938).

When compared at the same weight percent chlorine, all CPVCs have essentially the same set of 31Cl nmr chemical shifts. An easily observed feature of these spectra is the appearance of particular chemical shifts originating from sequences of unchlorinated PVC. Typically, a CPVC produced by the aqueous chlorination method, containing 69% by wt. Cl contains about 10–25% sequences of at least three unchlorinated VC units. In contrast, CPVC prepared by the high liquid chlorination process of this invention, and also containing 69% by wt. chlorine, contains essentially no detected sequences of three or more units of unchlorinated VC, that is, the CPVC of this invention is homogeneously chlorinated. In addition, it can be shown that the CPVC prepared by the aqueous process contains a much different distribution of
tactilities compared with that of CPVC prepared by this high liquid Cl₂ process. For example, at 65% by wt. Cl content, there are less than 10 mol% PVC sequences but the CPVC is nevertheless homogeneous. Also, as is described in greater detail hereinafter, the distribution of syndiotactic, heterotactic and isotactic peaks for desirable CPVC prepared by this high liquid Cl₂ process uniquely characterizes this material and identifies the process by which it is prepared.

Referring now to Fig. 1 there is schematically illustrated a jacketed reactor 10 made of suitable corrosion resistant material such as Hastelloy, designed to be operated at elevated pressure sufficient to ensure that liquid chlorine in the reactor is maintained in a liquid phase. The reactor 10 is equipped with ultraviolet lamps, identified by reference symbol L, of suitable intensity sufficient to photoliminate solid porous macrogranules of PVC suspended in the liquid Cl₂ to produce in the machine the Cl₂ and form CPVC which is dissolved in the liquid Cl₂. The reactor 10 is also equipped with a paddle-type stirrer 11 driven by an electric motor M₁ which keeps the suspension of PVC in liquid Cl₂ thoroughly agitated. In addition, the reactor is equipped with nozzles (not specifically identified) in its cover 12, to permit flushing it with an inert gas such as nitrogen when desired, and to carry off gaseous HCl generated during the chlorination reaction in which HCl some Cl₂ may be entrained. Nozzles 13 and 14 allow a lower temperature heat exchange fluid ("cryogen") to be introduced into, and discharged from, the jacket of the reactor so as to maintain its contents at any prescheduled temperature at the pressure chosen for its operation.

Liquid Cl₂ is charged to the reactor from a first Cl₂ cylinder 15 on a weigh scale 16, the amount of Cl₂ charged depending mainly upon the amount of solid PVC to be batch-chlorinated in the reactor. Since a more preferred temperature for chlorination is in the range from about –30°C to about 25°C, and still more preferably in the range from about –10°C to about 15°C, it is generally desirable to cool the Cl₂ drawn from the cylinder 15 in a heat exchanger 17 through which a cryogen from a refrigeration system R is circulated. After a period of time during which liquid Cl₂ is absorbed into the PVC macrogranules and swells them, ultraviolet lamps L in the reactor are turned on. Agitation is continued until the desired degree of chlorination is achieved, that is, a preselected level of Cl₂ is introduced into the PVC. This level is determined by simple trial and error.

The amount of Cl₂ vapor entrained with HCl evolved during reaction depends upon the process conditions chosen, particularly the pressure and temperature under which the reactor is operated. Where the entrainment of Cl₂ is significant, it is desirable to condense the Cl₂ vapors in a heat exchanger 18 through which cryogen from the refrigeration system R is circulated (connecting lines to R are not shown). The HCl vapors from the exchanger 18 are led to a HCl recovery system in which they are used as a reactant for another process. Liquid Cl₂ from exchanger 18 is returned by pump 19 to the reactor 10, to be reused.

Typically, the chlorination reaction is carried out batch-wise by charging a mass of macrogranules of PVC to the reactor, and commencing agitation to lower the temperature to about –10°C which is slightly higher than the temperature of the cooling fluid circulated through the reactor's jacket. A predetermined weight of liquid Cl₂ at about –10°C is then slowly pumped onto the churning mass of PVC macrogranules until the liquid Cl₂ having been absorbed by the mass of PVC macrogranules, floods them with an excess. The lamps L are then switched on and agitation continued. No catalyst other than the u-v light is either desirable or necessary. The progress of the reaction may be monitored by noting the amount and rate of HCl which is evolved from the reactor, zone of the reactor. When the reaction is essentially complete, as indicated by no further evolution of HCl, the agitation is stopped, and the CPVC formed is recovered. Runs at room temperature and corresponding pressure of about 6.895 × 10³ Pa (100 psig) are made in an analogous manner.

The contents of the reactor after chlorination is complete are generally syrupy, the consistency of the syrup depending primarily upon the ratio of liquid Cl₂ to PVC. The CPVC may be recovered from the syrup in any convenient manner. For example, the syrup may be thinned with tetrachloroethane (TCE), the Cl₂ driven from the thinned syrup, and the CPVC precipitated from its solution in TCE by concentration. A far more economical, novel and highly effective method is to thin the syrup with a halogenated lower alkane (HLA) in an amount sufficient to precipitate the CPVC.

For acceptable operation of the process of this invention, any HLA may be used provided, under operating conditions, (i) liquid Cl₂ is substantially completely soluble in the HLA, and (ii) CPVC is essentially insoluble in the HLA. By 'substantially completely soluble' I mean a solubility of at least 20 parts of liquid Cl₂ per 100 parts of HLA, and by 'essentially insoluble' I mean a solubility of less than about 100 parts per million (ppm).

A preferred HLA is chosen from among the chlorinated and/or fluorinated derivatives of a lower alkane having from 1 to about 6 carbon atoms, and more preferably from chlorinated and fluorinated derivatives of methane and ethane, and particularly mono- and di-chlorination products. Examples are selected from the mono- and di-chlorination products of methane, such as monochloromethane, dichloromethane, trichloromethane, tetrachloromethane, dichlorodifluoromethane ("CFC-22"), and chlorodifluorodichloromethane ("Freon12").

Brominated and iodo-compounds are also available as Freonz brand fluorocarbons from the E.I. du Pont de Nemours Co. More preferred are those fluoro-
carbons having a boiling point in the range from about -30°C to about 48°C, the particular fluorocarbon chosen depending upon its availability at reasonable cost, and the process conditions deemed most economical for its ability to dissolve liquid Cl₂ and be freed from it.

Soon after TCTFE is added to the reactor, the syrup becomes less viscous because of the essentially immediate dissolution of chlorine into TCTFE, making it easy to pump out the contents of the reactor. It has been found that an HLA derived from methane is not as easily freed from the CPVC formed as is an HLC derived from ethane. However, where freeing the HLA from the CPVC is not important, or where it may be desirable to have a significant concentration of the HLA remain with the CPVC, as for example where a cake of CPVC solids is converted to a CPVC foam, the methane derivatives, and in particular, DCDFM, may be preferred.

When TCTFE (commercially available as Freon-113®) is used, it is found that liquid TCTFE may be added to the contents of the preferably pressurized reactor, while stirring, causing Cl₂ to dissolve in the TCTFE and precipitating solid finely divided CPVC. The temperature of the TCTFE prior to its addition to the syrup is not critical but it is preferred that it be no higher than about 50°C even under pressurized conditions. It will be evident to one skilled in the art that, if desired, cold liquid DCDFM may be added to the syrup, or a gaseous HLA may be condensed into the syrup if the syrup is cold enough. The choice of optimum temperature at which the components CPVC, liquid Cl₂ and HLA form a three-component mixture in the reactor will be determined by the selection of the HLA and the economics of an energy balance.

Referring again to Fig. 1, after the CPVC is precipitated, dump valve 20 is opened and the three component mixture of HLA, liquid Cl₂ and solid CPVC is discharged into a suitable filter means such as a rotary filter 21, or alternatively to a centrifuge, to recover the CPVC as a filter cake of discrete finely divided solids. The filtrate is a solution of TCTFE and liquid Cl₂ which filtrate is pumped by a filtrate pump 22 to a recovery system for separating and recovering TCTFE and liquid Cl₂.

A preferred recovery system takes advantage of the considerably spread between the boiling points of TCTFE and liquid Cl₂ which allows Cl₂ to be easily stripped from the TCTFE in a Cl₂ stripper 30 provided with a suitable reboiler (not shown). Where DCDFM (Freon-12) is used, the Cl₂ may be recovered by simple distillation under pressure. The separation effected in either case is excellent since no azeotrope is formed between chlorine and either DCDFM or TCTFE. The Cl₂ and HLA are each recovered and each reused.

It is important that the HLA chosen as a solvent for liquid Cl₂ be added to the syrup-like solution of CPVC in Cl₂, or the morphology of the solid CPVC precipitated will not be the same. That is, the morphology of solid CPVC recovered by adding the HLA to the syrup will be different from the morphology of the solid CPVC recovered by adding the syrup to the HLA. The morphology of the solid CPVC affects its processability, and depending upon the processing requirements and properties sought in the finished article, the order of addition of syrup to solvent, or vice versa, is highly important.

Referring now to Fig. 2, there is shown a flowsheet schematically illustrating a continuous process of this invention. The PVC feed to be chlorinated enters at the inlet end 41 of a very long horizontal, jacketed reactor 40 which is equipped with a longitudinally axial helical agitator (referred to as a "votator") 42 with flights designed to lift macrogranules of PVC feed from near the bottom surface of the reactor to near the top, and to move any solids deposited near the bottom of the reactor towards its discharge end 43. In operation, the reactor may be viewed as having three zones, namely, a gel phase zone "G" near the inlet end, a reaction zone "R" in the mid-section, and a precipitation zone "PR" near the discharge end.

The PVC feed is continuously flowed into the reactor from a PVC storage bin 44, by being metered through a vaned metering device 45 driven by an electric motor M₁. The votator 42 is driven by an electric motor M₂ at a speed sufficient to churn the macrogranules soaking them in liquid Cl₂ held in the reactor, and thoroughly wetting their surfaces so as to form a gel phase on and within the macrogranules. The liquid Cl₂ is maintained at about 0°C in a storage tank 50 from which it is pumped by pump 51 to the reactor. The macrogranules of PVC are moved longitudinally slowly towards the reaction zone to afford sufficient time for the macrogranules to form the gel phase.

In the reaction zone there is provided above the votator 42 a bank of ultraviolet lights identified as
"L", which illuminate the PVC macrogranules and the gel phase PVC thereof while they are suspended in the liquid Cl₂, thus stimulating chlorination of the PVC to convert it to CPVC. As the chlorination reaction progresses, HCl gas is evolved, and because the reaction is exothermic, sufficient heat may be generated to evaporate some liquid Cl₂ from the reaction mass. Such evaporation of Cl₂ may help stabilize the reaction zone. The amount of Cl₂ evaporated may be controlled by maintaining a sufficiently low temperature in the reaction zone.

Byproduct HCl gas, and chlorine vapors are removed from the reaction zone and flowed to a heat exchanger 52 through which a low temperature coolant "cryogen", provided by refrigeration system 53, is circulated. The Cl₂ is condensed, and the HCl is recovered as gas which is used in another process.

Sufficient cold TCTFE from storage tank 56 is pumped with pump 57 to the precipitation zone P to precipitate essentially all the CPVC which is gradually moved towards the discharge end 43 and removed as a slurry. In a manner analogous to that described in Fig. 1 hereinbefore, the slurry is filtered, the solid CPVC is recovered, and the TCTFE and liquid Cl₂ separated and returned to the reactor for further use, the details of which are not shown in Fig. 2, and need not be repeated here.

Measurement of the glass transition temperature (Tg) at a particular chloride level (%Cl) of the CPVC, an analysis of its 13C nmr spectra, and evaluation of the results measured with a differential scanning calorimeter (DSC) indicate that homogeneous CPVC has a lower heat of melting corroborating its essentially non-crystalline nature. Referring now to the 13C nmr spectra shown in Figs. 3—7, which spectra were obtained with a Bruker Model No. WH-200 spectrometer operating at 50.28 MHz, and particularly first to Fig. 3, there is shown the spectra for PVC obtained by polymerization of vinyl chloride in an aqueous suspension which results in a PVC having 56.7% Cl. It is seen that the peaks corresponding to the CH₂ group are in the 46—48 ppm range relative to tetramethylsilane (0 ppm), and the peaks corresponding to the CHCl group are in the 55—58 ppm range (for additional details see the Carman article, supra).

The Tg of the PVC is 91°C as determined by the following method: A sample of about 10—15 mg is placed in the pan of Perkin Elmer DSC-2 and heated at the rate of 40°C/min. The Tg is computed from the midpoint of the transition curve generated in the second heating of the sample. The sharp Tg obtained is characteristic of well-defined off-repeated sequences characteristic of PVC.

After this PVC is chlorinated to 71.2% Cl in aqueous suspension as described in the US—A 2,969,489 to Dannis et al., its Tg is sufficiently broad to be indeterminate, indicating a large mix of sequences which undergo the glass transition phenomenon incrementally over a wide range of temperature. Referring to the CPVC spectra shown in Fig. 4, there is seen a peak identified by reference symbol A which corresponds to a CH₄-centered tetrad indicating the presence of syndiotactic sequences as in PVC evidenced in Fig. 3. Another peak identified by reference symbol B in Fig. 4 is also the same as that evidenced in PVC and corresponds to the CHCl-centered syndiotactic triad. The cluster of peaks C, D, E, F, G, H and I in the range from about 60—70 ppm are characteristic of a CPVC produced in aqueous suspension. An analogous cluster of peaks in this range of 60—70 ppm is found in any CPVC produced in aqueous suspension irrespective of how the PVC was derived. Other clusters of peaks in this range are also found in CPVC produced by fluid-bed chlorination with gaseous chlorine and with CPVC produced by my low liquid chlorination process disclosed in Serial No. 177,863, filed August 14, 1971.

Referring further to Fig. 4 there are also shown a cluster of peaks J, K and L in the range from about 87—97 ppm, and it is seen that the area under each of the peaks is progressively greater than that under the preceding one, the area under peak L being the greatest.

Referring now to Fig. 5 there is shown a representative spectra of the novel CPVC obtained by the high liquid chlorination process of this invention. The Tg is 184°C and not indeterminate indicating similar sequences having a well-defined Tg. The chloride content is 69.8% Cl which is substantially the same as that of the CPVC obtained by chlorination in aqueous suspension, no differences in structure being attributable to the slight difference in Cl content. A comparison of Fig. 5 with Fig. 4 shows no peak corresponding to peak A in Fig. 4 which indicates that no syndiotactic sequences are present in an amount sufficient to be detected. The cluster of peaks C—I in Fig. 4 are replaced with sharply defined peaks C', E', F', G' and I' in Fig. 5. Referring particularly to peaks J', K' and L' it is noted that the peaks are sharper and better defined than peaks J, K and L as is especially apparent with peaks J and L. Further, the combined areas under peaks J, K and L are clearly greater than the combined areas under J', K' and L' indicating that CPVC which gave the spectra in Fig. 5 is more homogeneously chlorinated than that which gave the spectra in Fig. 4.

It is further to be noted that Fig. 4 shows, in the range from about 37—45 ppm, a broad group of peaks which indicate a broad nmr absorption corresponding to CH₄ groups. This absorption is so broad that it fails to provide significant structural information about the CPVC. In comparison, the peaks M, N, O and P in Fig. 5 indicate the presence of at least four (4) different structural sequences containing CH₂ groups each of which is well-defined, indicating the homogeneity of the CPVC.

Referring now to Fig. 6 there is shown a representative spectrum of a CPVC containing 68.3% Cl obtained by solution chlorination of
PVC. As one would expect a solution chlorinated PVC to be homogeneously chlorinated, this spectrum (Fig. 6) is representative of a homogeneously chlorinated CPVC. In Fig. 6, the peaks M', N', O', and P' appear in the range of 37–45 ppm and correspond to the peaks M, N, O, and P in the same range in Fig. 5. However, specifically with respect to peaks N and N'; O and O'; and, P and P', a comparison indicates that in Fig. 6 peaks N' and O' are substantially equivalent but P' is clearly greater than either. In Fig. 5, P is the smallest of the four peaks, N being the greatest.

Referring now to the peaks in the range from about 57–70 ppm in Figs. 5 and 6, C' is the greatest peak in Fig. 5, clearly greater than F'. In Fig. 5, F' is the greatest peak, clearly greater than F'.

Referring now to Figs. 4, 5 and 6 for a comparison thereof with respect to peaks in the 57–70 ppm range, it is observed that H for aqueous chlorinated CPVC (Fig. 4) and H' for solution chlorinated CPVC (Fig. 6) appear at the initial stages of chlorination but does not appear for high liquid chlorinated CPVC (Fig. 5). Apparently the sequences which gave rise to a peak H' (not now visible in the spectra) are chlorinatable while the sequences which gave rise to peaks H and H' are not.

Examples

In a typical pilot plant run, 400 parts by wt. of macrogranules of Geon® 103EPF76 poly(vinyl chloride) resin having a Cl content of about 56.7% by weight, a general purpose resin, are charged to the jacketed reactor fitted with a helical paddle stirrer, and a bank of ultraviolet lights some or all of which may be turned on, as desired. Liquid cryogen, such as a chilled brine solution, is circulated through the jacket of the reactor so as to keep chlorine in the liquid state at the pressure and temperature at which the chlorination reaction is to be carried out. After charging the reactor with PVC the reactor and its contents are subjected to vacuum, or flushed with an inert gas, preferably nitrogen. Thereafter, liquid chlorine is sprayed into the reactor while the macrogranules of PVC are being slowly churned by the paddle stirrer, until 4000 parts of liquid Cl₂ are charged.

The PVC macrogranules form a slurry which is easily agitated by the paddle stirrer in the reactor.

After a short period of about 30 mins or less, which is not critical, it is found that most of the macrogranules have swollen. In this swollen condition they are ready for photoclination which is affected by turning on the bank of ultraviolet lights. The lights are left on for as long as is required to produce the desired Cl content in the CPVC, this time being arrived at by trial and error for the particular temperature and pressure conditions of the reactor. The period of irradiation is in the range from about 4 to about 8 hours depending upon the particular physical characteristics of the PVC, and the intensity of the lights. A more preferred time for irradiation is in the range from about 5 to about 6 hours. While the slurry of PVC in liquid Cl₂ is being irradiated, it is continuously slowly stirred to facilitate evolution of HCl and Cl₂ from the reaction mass, and to permit more uniform chlorination of the PVC. For economic reasons the preferred temperature of operation is in the range from about 0°C to about 35°C, and the chlorine evolved is condensed and returned to the reactor for another run; the HCl evolved is recovered for use in another reaction.

At the end of the reaction, a thick syrupy solution of CPVC in liquid Cl₂ ("syrup") is obtained which is thinned with five times as much TCTFE as there is syrupy solution in the reactor, the TCTFE being precooled below temperature, preferably in the range from about 0°C to about 10°C. After substantially all the CPVC is precipitated from solution, the contents of the reactor are discharged to a rotary filter from which solid CPVC is removed and dried to rid it of the TCTFE-liquid Cl₂ solution which wets the cake. About 515 parts dry finely divided solid CPVC in the size range from 325 mesh and smaller, to 6 mesh and larger, U.S. Standard, are recovered indicating that essentially all the PVC has been converted.

The surface area of the PVC starting material in Table I, measured by the BET method, is in the range from about 1.26 to about 1.75 m²/g, and the surface area of the CPVC obtained is generally less, the decrease in surface area being characteristically in the range from about 20 to about 50%, depending upon the particular process conditions for chlorination and the method of recovery of the CPVC formed. The results obtained by chlorination in an analogous manner as above, are tabulated in Table I hereinbelow:
<table>
<thead>
<tr>
<th>PVC Resin identified</th>
<th>Surface area of PVC m²/g</th>
<th>PVC Resin charged g</th>
<th>Liquid Cl₂ charged g</th>
<th>Ratio Cl/PVC</th>
<th>Ultraviolet light used</th>
<th>Chl'n't'n time mins.</th>
<th>% Cl₂ in CPVC</th>
<th>T₁ g °C</th>
<th>TGA* 10% wt. loss, at °C</th>
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<td>100</td>
<td>500</td>
<td>5.</td>
<td>PenRay</td>
<td>300</td>
<td>66.9</td>
<td>145</td>
<td>307</td>
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<td>600</td>
<td>6.</td>
<td>300 w</td>
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<td>300 w</td>
<td>360</td>
<td>65.5</td>
<td>130</td>
<td>308</td>
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<tr>
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<td>500</td>
<td>10</td>
<td>60 w</td>
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<td>71.6</td>
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<td></td>
</tr>
<tr>
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<td>375</td>
<td>15</td>
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<td>69.9</td>
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</tr>
<tr>
<td>103EP</td>
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<td>25</td>
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<td>20</td>
<td>PenRay</td>
<td>360</td>
<td>70.5</td>
<td>194</td>
<td>340</td>
</tr>
</tbody>
</table>

* thermal gravimetric analysis under nitrogen.
** code for Geon* brand PVC resins manufactured and sold by the B. F. Goodrich Company.
* Geon is a Trademark of the B. F. Goodrich Company.
Claims

1. A process for photochlorinating poly(vinyl chloride) homopolymer ("PVC") of high molecular weight macrogranules to obtain homogeneously chlorinated 'chlorinated poly(vinyl chloride)' ("CPVC"), comprising,
(a) suspending said homopolymer having a chlorine content in the range from 55% to 57% by weight, in liquid chlorine present in an amount at least 5 times the weight of said homopolymer, for a period of time sufficient to absorb said liquid chlorine into said macrogranules,
(b) swelling said macrogranules at solid-liquid interfaces within and around said macrogranules to produce a gel phase by the action of said liquid chlorine,
(c) photo-illuminating said gel phase with actinic radiation until said homopolymer is converted into a homogeneously chlorinated CPVC having at least 65% by weight of chlorine, and the mol ratio of PVC present in a sequence of 3 or more vinyl chloride units, to the mols of total vinyl chloride units, is always less than 0.30,
(d) obtaining a solution of said homogeneously chlorinated CPVC in liquid chlorine, and,
(e) recovering solid homogeneously chlorinated CPVC from said solution.

2. The process of claim 1 wherein recovering solid homogeneously chlorinated CPVC from said solution comprises,
(i) adding a halogenated lower alkane to said solution in an amount sufficient to dissolve said liquid chlorine,
(ii) precipitating said solid homogeneously chlorinated CPVC from said liquid chlorine and halogenated lower alkane.

3. The process of claim 1 wherein said liquid chlorine is present in an amount from 5 to 50 times the weight of said homopolymer.

4. The process of claim 1 wherein said liquid chlorine is present at a temperature in the range from -50°C to 50°C.

5. The process of claim 1 wherein said PVC has a molecular weight in the range from 100,000 to 1,000,000.

6. The process of claim 1 wherein said CPVC as a chlorine content in the range from 65 to 73 percent by weight.

7. The process of claim 1 wherein recovering said solid homogeneously chlorinated CPVC from solution comprises,
(i) adding a sufficient amount of a halogenated lower alkane selected from the group consisting of dichlorodifluoromethane and trichlorotrifluoroethane to said solution to precipitate substantially all said homogeneously chlorinated CPVC as solid, and
(ii) separating precipitated solid from said halogenated lower alkane and liquid chlorine.

8. Solid CPVC resin having
(i) a chlorine content greater than 65 percent by weight,
(ii) a determinable glass transition temperature,
(iii) in a 1H nuclear magnetic resonance spectrum of said CPVC, a first peak at about 41 ppm said first peak being greater than other peaks in the range from 37 to 45 ppm, and
(iv) a second peak at 63 ppm, said second peak being greater than other peaks in the range from 57–70 ppm.

9. The solid CPVC of claim 8 wherein said chlorine content is at least 70 percent by weight, and, said spectrum has no detectable syndiotactic peak in the range from 45–50 ppm.

10. Solid CPVC obtained by
(a) suspending macrogranules of PVC having a chlorine content in the range from 55% to 57% by weight, in liquid chlorine present in an amount at least 5 times the weight of said homopolymer, for a period of time sufficient to absorb said liquid chlorine into said macrogranules,
(b) swelling said macrogranules at solid-liquid interfaces within and around said macrogranules to produce a gel phase by the action of said liquid chlorine,
(c) photo-illuminating said gel phase with actinic radiation until said homopolymer is converted to homogeneously chlorinated CPVC having at least 65% by weight of chlorine, and the mol ratio of PVC present in a sequence of 3 or more vinyl chloride units, to the mols of total vinyl chloride units, is always less than 0.30,
(d) obtaining a solution of said homogeneously chlorinated CPVC in liquid chlorine, and,
(e) recovering solid homogeneously chlorinated CPVC from said solution.

Patentansprüche

1. Verfahren zur Photochlorierung von Makrogranulat aus einem Poly(vinylchlorid)-Homopolymer ("PVC") mit hohem Molekulargewicht zur Gewinnung eines homogen chlorierten 'chlorierten Poly(vinylchlorid)' ("CPVC") durch
(a) Suspendieren des Homopolymers mit einem Chlor-Gehalt im Bereich von 55 bis 57 Gew.-% in flüssigem Chlor, das in wenigstens der fünffachen Gewichtsmenge des Homopolymers vorliegt, während einer für die Absorption des flüssigen Chlors in dem Makrogranulat ausreichenden Zeitspanne,
(b) Quellen des Makrogranulats an den Grenzflächen Feststoff-Flüssigkeit im Inneren und um das Äußere des Makrogranulats herum unter Bildung einer Gel-Phase unter der Einwirkung des flüssigen Chlors.
(c) Photo-Beleuchten der Gel-Phase mit aktinischer Strahlung, bis das Homopolymer in eine homogen chloriertes CPVC mit wenigstens 65 Gew.-% Chlor umgewandelt ist und das Stoffmengen-Verhältnis ("Mol-Verhältnis") des in einer Sequenz von 3 oder mehr Vinlychlorid-Einheiten vorliegenden PVC zu der Stoffmenge der insgesamt vorhandenen Vinlychlorid-Einheiten stets kleiner als 0,30 ist,
(d) Gewinnen einer Lösung des homogen chlorierten CPVC in flüssigem Chlor und
(e) Isolieren des festen, homogen chlorierten CPVC aus dieser Lösung.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Isolierung des festen, homogen chlorierten CPVC aus dieser Lösung das
(i) Zugeben eines halogenierten niederer Alkan zur Lösung in einer zum Auflösen des flüssigen Chlors ausreichenden Menge,
(ii) Ausfällen des festen, homogen chlorierten CPVC und
(iii) Abtrennen des festen, homogen chlorierten CPVC von dem flüssigen Chlor und dem halogenierten niederer Alkan umfaßt.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das flüssige Chlor bei einer Temperatur im Bereich von −50°C bis 50°C vorliegt.

5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das PVC ein Molekülge wicht in dem Bereich von 100 000 bis 1 000 000 besitzt.

6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das CPVC einen Chlor-Gehalt in dem Bereich von 65 bis 73 Gew.-% aufweist.

7. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Isolierung des festen, homogen chlorierten CPVC aus dieser Lösung das
(i) Zugeben eines aus der aus Dichlorodi-
fluoromethan und Trichlorotrifluoroethan bestehenden Gruppe ausgewählten halogenierten niederer Alkanen zu der Lösung in einer zum Ausfallen der im wesentlichen gesamten Menge des festen, homogen chlorierten CPVC als Feststoff ausreichenden Menge und
(ii) Abtrennen des ausgefallenen Feststoffs von dem halogenierten niederer Alkan und dem flüssigen Chlor umfaßt.

8. Festes CPVC-Harz mit
(i) einem Chlor-Gehalt von mehr als 65 Gew.-%,
(ii) einer bestimmten Glasübergangs-

9. Festes CPVC nach Anspruch 8, dadurch gekennzeichnet, daß der Chlor-Gehalt wenigstens 70 Gew.-% beträgt und das Spektrum keinen nachweisbaren syndiotaktischen Peak im Bereich von 37 bis 45 ppm und
(iv) einem zweiten Peak bei 63 ppm, wobei dieser zweite Peak größer ist als andere Peaks im Bereich von 57 bis 70 ppm.


10. Festes CPVC, erhalten durch
(a) Suspendieren eines Makrogranulats aus PVC mit einem Chlor-Gehalt im Bereich von 55 bis 57 Gew.-% in flüssigem Chlor, das in wenigstens der fünfzehn Gewichtsmenge des Homopolymers vorliegt, während einer für die Absorption des flüssigen Chlors in dem Makrogranulat ausreichenden Zeitspanne,
(b) Quellen des Makrogranulats an den Grenzflächen Feststoff-Flüssigkeit im Inneren und um das Außen des Makrogranulats herum unter Bildung einer Gel-Phase unter der Einwirkung des flüssigen Chlors,
(c) Photo-Beleuchtung der Gel-Phase mit aktinischer Strahlung, bis das Homopolymer in ein homogen chloriertes CPVC mit wenigstens 65 Gew.-% Chlor umgewandelt ist und das Stoffmengen-Verhältnis des in einer Sequenz von 3 oder mehr Vinilchlorid-Einheiten vorliegenden PVC zu der Stoffmenge der insgesamt vorhandenen Vinilchlorid-Einheiten stets kleiner als 0,30 ist,
(d) Gewinnen einer Lösung des homogen chlorierten CPVC in flüssigem Chlor und
(e) Isolieren des festen, homogen chlorierten CPVC aus dieser Lösung.

Revendications

1. Procédé de photochlorination de macrogranulés de poly(chlorure de vinyle) homopolymeres ("PVC") de masse moléculaire élevée, pour obtenir un "poly(chlorure de vinyle) chloré" ("PVC"), chloré d'une manière homogène, consistant
(a) à mettre en suspension ledit homopolymère, ayant une teneur en chlore dans la gamme de 55 à 57% en poids, dans du chlore liquide présent en une quantité au moins égale à cinq fois le poids dudit homopolymère, pendant une période de temps suffisante pour provoquer l'absorption dudit chlore liquide dans lesdits macrogranulés,
(b) à faire gonfler lesdits macromolécules, aux interfaces solide-liquide, à l'intérieur et autour desdits macrogranulés, pour produire une phase gel sous l'action dudit chlore liquide,
(c) à soumettre ladite phase gel, à un rayonnement actinique, jusqu'à ce que ledit homopolymère soit converti en CPVC chloré d'une manière homogène possédant au moins 65% en poids de chlore, le rapport entre le nombre de moles de PVC présentes dans une séquence d'au moins trois motifs chloruré de vinyly et le nombre de moles total de motifs chloruré de vinyly, étant toujours inférieur à 0,30,
(d) à obtenir une solution dudit CPVC chloré d'une manière homogène dans du chlore liquide, et
(e) à récupérer de ladite solution le CPVC solide chloré d'une manière homogène.

2. Procédé selon la revendication 1, dans lequel
(a) la récupération du CPVC solide chloré d'une manière homogène, à partir de ladite solution, consiste
(i) à ajouter un alcane inférieur halogéné à ladite solution, en une quantité suffisante pour dissoudre ledit chlore liquide,
(ii) à faire précipiter ledit CPVC solide chloré d'une manière homogène, et
(iii) à séparer dudit chlore liquide et de l'alcane inférieur halogéné ledit CPVC solide chloré d'une manière homogène.

3. Procédé selon la revendication 1, dans lequel...
ledit chlore liquide est présent en une quantité de 5 à 50 fois le poids dudit homopolymère.
4. Procédé selon la revendication 1, dans lequel ledit chlore liquide est présent à une température dans la gamme de −50°C à 50°C.
5. Procédé selon la revendication 1, dans lequel ledit PVC a une masse moléculaire dans la gamme de 100 000 à 1 000 000.
6. Procédé selon la revendication 1, dans lequel ledit CPVC a une teneur en chlore dans la gamme de 65 à 73% en poids.
7. Procédé selon la revendication 1, dans lequel la récupération dudit CPVC solide chloré d’une manière homogène à partir de la solution consiste
   (i) à ajouter une quantité suffisante d’un alcane inférieur halogéné, choisi dans le groupe comprenant le dichlorodifluorométhane et le trichlorotrifluoroéthane, à ladite solution pour faire précipiter la presque totalité dudit CPVC chloré d’une manière homogène, sous la forme d’un solide, et
   (ii) à séparer le solide précipité dudit alcane inférieur halogéné et dudit chlore liquide.
8. Résine de CPVC solide ayant
   (i) une teneur en chlore supérieure à 65% en poids,
   (ii) une température de transition vitreuse déterminable.
   (iii) dans un spectre de résonance magnétique nucléaire $^{13}$C dudit CPVC, un premier pic à environ 41 ppm, ledit premier pic étant plus haut que les autres pics dans la gamme de 37 à 45 ppm, et
   (iv) un deuxième pic à 63 ppm, ledit deuxième pic étant plus haut que les autres pics dans la gamme de 57 à 70 ppm.
9. CPVC solide selon la revendication 8, dans lequel ladite teneur en chlore est d’au moins 70% en poids, et ledit spectre ne présente aucun pic syndiotactique décelable dans l’intervalle de 45—50 ppm.
10. CPVC solide obtenu
   (a) en suspendant des microgranulés de PVC ayant une teneur en chlore dans la gamme de 55 à 57% en poids dans du chlore liquide présent en une quantité d’au moins cinq fois le poids dudit homopolymère, pendant une période de temps suffisante pour provoquer l’absorption dudit chlore liquide par lesdits macrogranulés,
   (b) en faisant gonfler lesdits macrogranulés aux interfaces solide-liquide à l’intérieur et autour desdits macrogranulés pour produire une phase gel sous l’action dudit chlore liquide,
   (c) en soumettant ladite phase gel à un rayonnement actinique jusqu’à ce que dudit homopolymère soit converti en CPVC chloré d’une manière homogène et ayant au moins 65% en poids de chlore, le rapport entre le nombre de moles de PVC présentes dans une séquence d’au moins trois motifs chlore de vinylyle et le nombre total de moles de motifs chlore de vinylyle étant toujours inférieur à 0,30,
   (d) en obtenant une solution dudit CPVC chloré d’une manière homogène dans du chlore liquide, et
   (e) en récupérant de ladite solution le CPVC solide chloré d’une manière homogène.