

Investigating Surface Properties of Functional Polymers

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Research work in this paper on the synthesis of polymers is developing on the development of scientific principles for creating new functional polymers. The paper has accumulated experience in developing polymer properties containing chemically active functional groups in their structure, researching their structure and morphology, and showing the prospects for their application in several priority areas of science and technology development, such as membrane technology, microelectronics, biotechnology, and ecology. The work's main goal is to develop methods for the directed synthesis and modification of polymers and materials based on them with a given structure (including nanostructure) and morphology.

Introduction

During the preparation of polymers, it seems that the reaction of transfer of the active site from the OH radical to the polymer chain with the detachment of the hydrogen atom, the resulting polymer radicals can either initiate further chain growth with the formation of branched molecules or recombine with the primary OH radicals present in the system in excess. The latter reaction leads to an increase in the functionality of the polymer without changing its molecular weight. The expression of functional polymers does not have that precisely defined meaning, which is usually implicit in scientific terms. The word functionality in application to natural and synthetic polymers has an extremely broad meaning.

Background Information

Since ancient times, humankind used various materials for survival, the first functional characteristics of which, apparently, were thermal conductivity and mechanical strength. More than 5000 years ago, in India and China, people began using natural polymers such as cotton (cellulose), silk (polyamide), etc. In the modern era, synthetic materials have been added to natural polymeric materials, and now polymer products form an integral part of our environment. Synthetic materials, by their characteristics, often significantly exceed natural, and in many areas, they have already supplanted the latter. This process continues before our eyes. As an example, you can point to the emergence of electrical insulation coatings made of polyvinyl chloride, vessels made of polypropylene, laboratory equipment made of Teflon, glasses made of polymethylmethacrylate, and much more. Based on temperature characteristics, chemical resistance, and electrical and mechanical properties, new materials significantly exceed all previously known.

Significance

The polymers produced in the industry contain cyclic compounds that sharply reduce the number average molecular weight and thereby reduce the functionality of the polymers. The introduction of a correction to the value of the number-average molecular weights of the polymer for the content of cyclic molecules in it and their molecular masses makes it possible to determine the functionality of the chain part, which corresponds to the calculated values.

Thesis statement

Synthesis and study of the properties of so-called functional polymers are among modern science's most important areas of development. (Hetemi & Pinson, 2017; Spychalska et al., 2020)

Catalysis on specific polymer surfaces and in molecular imprints

Suppose bifunctional catalysis occurs at neutral or close to neutral pH values, i.e., the interaction between uncharged imidazole groups. In that case, three mechanisms can be proposed to describe the interactions between a polymer catalyst and a substrate.

Catalytic processes are widespread in nature and are effectively used in various industries, science, and technology. Thus, in the chemical industry, tens of millions of tons of ammonia are produced from heterogeneous catalytic processes from air nitrogen and hydrogen, nitric acid by oxidation of ammonia, sulfur trioxide by oxidation with 50 g of air, etc. In the petrochemical industry, more than half of the oil produced by catalytic processes of cracking, reforming, etc., is processed into more valuable products – high-quality motor fuel, various monomers for the production of polymeric fibers, and plastics. Multi-tonnage catalytic processes include the processes of hydrogen production by conversion of carbon dioxide and methane, the synthesis of alcohols, formaldehyde, and many others. It can be argued that a catalyst can be created for any reaction. The theory of catalysis should disclose the regularities of an elementary catalytic act, the dependence of catalytic activity on the structure and properties of the catalyst and the reacting molecules, and thus create the necessary prerequisites for predicting the structure and properties of the catalyst for a particular reaction, and indicate the ways of its production. The description of the rate of the catalytic process can be approached using the main provisions of formal kinetics and the transition state method. At the same time, it is expedient to isolate the general laws of catalysis inherent in all types of catalytic processes first and then consider some specific features of individual groups of catalytic processes.

One of the problems of molecular bionics – is the creation of polymeric catalysts for various reactions, which operate on the principle of enzymes and approach the enzymes on the activity and selectivity

of action. (BelBruno, 2019; Spychalska et al., 2020) It is well known that enzymes are incommensurably more productive than the best catalysts of non-biological origin used by the chemical industry. It is also clear that proteins are very complex molecular structures, and the precise reproduction of these by non-biological methods is a very difficult task. Overcoming the huge gap between synthetic and biopolymers in the foreseeable future until recently seemed almost impossible. At the same time, there is no need to prove how attractive the prospect of designing artificial non-protein enzymes that are tuned to the catalysis of practically important reactions is. This would make it possible, with colossal efficiency, to obtain industrially important products in small reaction volumes and without significant energy costs. The decisive role in the development of the production of HDPE, as before, remains behind the catalysts. In recent years, the search for catalytic systems has been fundamentally different from the known ones. For such systems, I am, in particular, immobilized on polymeric supports (heterogenized catalyst systems) of significant interest – component catalysts operating at PO- Vyshen temperatures (up to 200 ° C) and functional catalysts. Studies in the field of highly active catalytic olefin polymerization systems adjoin the general problem of catalysis – the use of catalytic systems is close to [1x to biocatalysts-enzymes.

The above examples relate to homogeneous systems in which both the starting materials and polymer catalysts dissolve uniformly. Such systems are very convenient for studying reaction mechanisms, the main regularities of catalysis by polymer additives, etc. However, in this case, it is always difficult to separate the reaction products and catalysts. For production goals, insoluble polymer catalysts are more promising.

An example of such a substance is ion exchange resins. Columns filled with sulfonated polystyrene have been used for the hydrolysis of esters since 1960. At the same time, the course of the reaction is almost independent of the flow rate of the reacting liquid but is related to the size of the resin beads. The catalytic effect is determined mainly by the rate of diffusion inside the polymer beads and not by the polymer's proper nature. For comparison, we give the ratio of the catalytic efficiency of a cation exchange resin and a low molecular weight catalyst (sulfuric acid) for several reactions. This value is 0.5 for methyl acetate, 0.3 for ethyl acetate, and 0.05 for ethyl-n-caproate. A lot of data is known about the advantages (in comparison with catalysis with low molecular weight agents) of catalysis by polymer additives in heterogeneous systems of esterification, alcoholysis, condensation of acetals, inversion of sugars, etc.

Absorption and wetting behavior of polymers

In industry, a wet coating is usually carried out with an aqueous solution of a suitable acid salt. Sodium salt is used most often, although this leads to the appearance of some amount of residual sodium in the product; this can be a problem if water absorption and electrical stability are important. Ammonium salts have the advantage that they do not leave any cationic residue; ammonia is eliminated at the stage of coating formation or during drying. The yield of ammonia, however, may present a problem when handling the material. Again, certain measures should be taken if free salt

formation is to be avoided.

The adsorption of fatty acids on polar surfaces is well studied; as a rule, it leads to the forming of a layer of carboxyl groups on the surface, with the carbon chains oriented normally to the surface. (Kasalkova et al., 2015; Hetemi & Pinson, 2017) If the surface at the microscopic level is sufficiently smooth, and the chains are sufficiently long, then the layer can be considered semicrystalline. With such packaging, the area occupied by one molecule of saturated linear fatty acid is about 0.21 nm². Fatty acids with branched chains, as well as those that contain double bonds, do not allow such a dense packing and, therefore, occupy a large surface area. It is believed that such surfaces are formed on mineral fillers but with the conversion of the acid group to carboxylate. The conversion of isostearic acid to its carboxylate is illustrated by changes in the IR Fourier spectra in Fig. 1. Monolayer adsorption levels are often correlated with those predicted based on the known surface area of the fillers and the area occupied by one surfactant molecule.

Changes in the properties of composites are often maximum at a coating thickness close to the monolayer if it is correctly formed. For example, the impact strength of a PP homopolymer filled with calcium carbonate is maximized with a monolayer coating. Roton et al. The effect produced by coatings from stearic acid on magnesium hydroxide in an ethylene-vinyl acetate copolymer (18% vinyl acetate) was studied in detail. The fracture elongation increased, and the tensile strength and modulus decreased until reaching a monolayer level. Interestingly, an excess of the coating above the monolayer increased the rate of aging of the composite (loss of properties at room or elevated temperature), with the industrial mixture of fatty acids having a stronger deteriorating effect than pure acid.

Degradation and thermal behavior of polymers

Thermal degradation of polymers is usually a free radical process. (Pielichowski et al., 2023) The chain break can occur either by the law of the case or by weak points (for example, near branches or structural irregularities) or at the ends of the chain. Thermal degradation of a number of polymers (for example, polyethylene, polypropylene, polyacrylic acid esters, polyacrylonitrile, and polybutadiene) does not lead to the formation of a monomer. In these cases, proper degradation proceeds. If the main product of degradation of the polymer is a monomer. For example, the processing of polyvinyl chloride in products, yarns, and films is fraught with great difficulties, which is explained by the low temperature of thermal degradation of the polymer, close to the temperature range in which plastic deformation of polyvinyl-polypropylene withstands the action of 98% sulfuric acid at a temperature of 90 for 7 hours, it varies at 70 in 50% nitric acid, is not destroyed in concentrated hydrochloric acid and 40% sodium hydroxide solution. Under the influence of air oxygen, polypropylene is gradually oxidized, especially during the molding of articles at elevated temperatures. Oxidation is accompanied by an increase in rigidity and then the brittleness of the material. The introduction of antioxidants (phenols, amines) into polypropylene stabilizes the properties of the polymer, which has been in the molten state for several hours. Long-term sun

exposure gives polypropylene fragility, speeding up the process of oxidative degradation. The introduction of an antioxidant and soot into polypropylene improves the resistance of polypropylene to light. Thermal degradation of the polymer is observed above 300.

The industry produces the following polyvinylchloride: PB-1, PB-2, PB-3, and PB-4, with a viscosity of 2 to 1.3 sst. Polyvinylchloride is characterized by low heat resistance. At a temperature above 145 °, the thermal degradation of the polymer begins due to the elimination of hydrogen chloride. The latter accelerates the further destruction of the polymer, so thermal destruction usually proceeds at an ever-increasing rate. In the initial period of polymer heating, the polymer chains are also broken, which increases the plasticity of the polymer.

In the thermal destruction of polymers, along with a decrease in the average molecular weight and a change in the structure of the polymer, the monomer is cleaved off by depolymerization. The yield of the monomer (Table 16) depends on the nature of the polymer, the conditions for its synthesis, and thermal decomposition.

Above 350, slow thermal degradation of the polymer begins with the release of fluorine. Below this temperature, the plasticity of the polymer is negligible, and it is impossible to dry the molding of the articles. Therefore, the fluoroplastic is processed by the sintering method. The fluoroplastic powder in cold forms is molded into tablets at a pressure of 200-300 kg cm. Tablets are installed in special-purpose furnaces and heated at 360-380 ° until the powder particles are completely sintered in them.

An interesting regularity relates the nature of the degradation products to the heat of polymerization of these compounds during the thermal destruction of polymers containing quaternary carbon atoms in the chain and having a low value of the heat of polymerization, mainly a monomer is formed. If the polymer contains secondary and tertiary carbon atoms in the chains and has a high value of the heat of polymerization, then under thermal degradation, the monomer is almost not formed, and the process ends with the formation of stable macromolecules with a reduced molecular mass (Table 15.1).

Thermal destruction of polymers is used for analytical purposes to study the structure of polymeric macromolecules, both chemical and spatial, as well as to evaluate the sequence of sequences of monomeric units in macromolecules. For this, chromatographic, and spectral analysis methods (for example, gas chromatography, IR and UV spectroscopy, mass spectrometry, etc.) are used.

So, the thermostability of polymers is one of the most important characteristics of their serviceability. (Pielichowski et al., 2023) The decomposition of polymers under thermal action leads to a sharp drop in their physico-mechanical properties and the release of low-molecular products, often toxic and fire-hazardous. Knowledge of the mechanism of thermal destruction of polymers allows for choosing the ways of their stabilization and, hence, the prolongation of the life of products from polymers. The predominant process is the thermal destruction of polymers, which depends on the chemical nature of polymers by the mechanism of random rupture of macromolecules or depolymerization. The increase in the thermal stability of polymers is associated with the methods of inhibition of these reactions or

the synthesis of more thermally stable polymer structures.

The possibility of carrying out nonequilibrium polycondensation in solution or under conditions of an interphase version, under mild conditions, often at low temperatures close to room temperature, allows the use of thermally unstable monomers in the polycondensation process, retains unsaturated and other reactive groups in the resulting macromolecules, avoid thermal degradation of the polymers in the process synthesis. This, in particular, opened the way for the successful production of polymers with high melting points.

Temperature Of Beginning Of Intensive Thermal Destruction Of Polymers

The temperature has begun intensive thermal destruction of polymers 219. Mass spectrometry in polymeric chemistry is used to study the stereoregularity of polymers by thermal decomposition of macromolecules and the analysis of evolved gases in the study of thermal destruction of polymers (pyrolysis) by analyzing the evolved gases (Section 34.14) for determining gas-permeability constants.

Thermogravimetry is used in polymer chemistry in the study of thermal destruction of polymers (kinetics and mechanism of destruction), thermal stability of polymers, oxidative degradation, solid-phase reactions, moisture determination, volatility and ash, absorption, adsorption and desorption, volatility of plasticizers, plastics and composite materials, identification of polymers.

Thermal analysis of volatile substances is one of the methods for determining evolved gases, which consists of measuring the pressure of gases produced during the thermal destruction of polymers.

The development of injection molding machines did not stop at worm plasticization. Gradually, these machines were improved by the latest achievements in this area, which were low-pressure casting machines or autogenous injection molding machines (Flow molding, Fliessgiessen). The principle of their action is that the processed material is rotated by a combined action of hydraulic pressure and high shear rates. Immediately after achieving the necessary fluidity and temperature, when the worm moves toward the hopper, an injection nozzle opens with a stopcock. The worm begins to fill the mold with a plasticized polymer under constant pressure, supported by a hydraulic cylinder. This ensures a constant melt temperature. After casting the shape, the worm retreats to the rear position, which is set so that the excess of the melt suffices just to compensate for the shrinkage due to the cooling of the plastic in the mold. In this position, the rotation of the worm ceases, and at the same time, it switches to holding under pressure so that the worm produces a form feed like a piston. After complete cooling, a molded connector is made, and the finished casting is extracted. The main advantage of such machines is the ease of adjusting the temperature of the material with the help of internal shear and hydraulic pressure. Both factors provide relatively reliable control of the plasticization process without fear of thermal destruction of the polymer when filling the molds.

As light sources, lasers and high-resolution optics are used. For the most common helium-neon laser, the exposure times are 1/50 s. Weaker scattering patterns can be detected using more intense lasers (ionic argon or cadmium lasers), but with increasing laser power, thermal degradation of the polymer can develop.

There are two more methods of experimental studies of the thermal destruction of polymers, which should be briefly mentioned in connection with the fact that, from time to time, they attract a lot of attention. We are talking about flash pyrolysis and calculating the kinetic parameters from the data of thermal analysis.

At a temperature of 270 ... 280 ° C, the pyrolysis proper stage begins, which ends at about 400 ° C. At this stage, exothermic reactions of thermal degradation of wood polymers take place with the release of a large amount of heat and the formation of the bulk of gaseous and liquid decomposition products, first of all, CO₂, CO, other non-condensable gases, acetic acid, methanol, and then resins. In the remainder of pyrolysis, charcoal is produced.

Thermal destruction of polymers

In the thermal destruction of polymers in air, oxidation reactions prevail over degradation reactions, so it is often completely unclear what causes the reaction.

The use of pyrolytic gas chromatography is limited by the complexity of chemical reactions during pyrolysis. In addition, the composition of pyrolysis products depends on the conditions of its conduct (temperature, duration, sample size, the velocity of carrier gas, etc.). To obtain reproducible test results, the test conditions must be strictly standardized. Thermal degradation of the polymer is sensitive even to small changes in pyrolysis conditions. The determining parameters of the process are the magnitude and geometric shape of the hydrolyzable sample, the temperature regime and duration of pyrolysis, and the conditions for chromatographic separation.

The degree of degradation also depends on the concentration of the polymer in the oil and on the duration of the mechanical action of the thermal action. The only possible way to combat mechanical destruction is the use of a relatively low mole for thickening polymers. Weight (3000-5000). To prevent the thermal destruction of polymers in the oil, add Misaki. Typically, antioxidative psadki are used for this purpose (Table 11. 7 and Fig. 4).

All organic polymer compounds are burned or charred at a high temperature. At 250-450, thermal degradation of polymers is usually observed, which can be associated with the cleavage of substituents and hydrogen atoms from two neighboring carbon atoms in macromolecules and the appearance of double bonds in them. Therefore, this process of destruction is often accompanied by the combination of individual macromolecules with polymer chains.^{1'1} Another type of thermal destruction is due to the breakdown of the bond between the atoms in the main chain of the macromolecule and the formation of lower molecular weight polymers (demo and In many cases, both

processes take place simultaneously.

Many polymers undergo oxidation at elevated temperatures. The oxidative reaction can be easily established by comparing the DTA curves obtained by directly heating the sample in air and in an inert gas atmosphere. Thus, the oxidation of HDPE at elevated temperatures, according to NA, Nechitailo, and others, is shown in Fig. 1.Yu. The oxidation reaction corresponds to a wide exothermic region, covering the temperature range from 160 to 450 ° C. Under the nitrogen atmosphere (curve 2), the exothermic reaction is completely absent. The endothermic peak at 500 ° C corresponds to the thermal degradation of the polymer, and its position does not depend on the atmosphere in which the heating is carried out.

The temperature of intensive thermal destruction of polymers has begun at 217

Kinetic consideration of the chain radical process of thermal destruction of a polymer includes the steps of initiation, growth of a reaction chain, transfer of a chain, and breakage thereof. The chain transfer reaction proceeds mainly due to the detachment of hydrogen from the polymer chain, which is connected to polymers containing [. The literature also describes the so-called thermal destruction of a polymer, which was studied, in particular, by Wisserot (Table 8.2).

Even if the thermomechanical curve has a classical form (see Figure 18) and consists of three sections, one should refrain from the assertion that the polymer possesses all three physical states, passing from one to another under heating. It should be borne in mind that the increase in strain in a powder sample can be caused by side effects. Having determined the thermomechanical curve, it is better to first pay attention to the last branch of the curve. If this branch is in the temperature range where the thermal or thermal-oxidative destruction is not yet deep enough, one can talk about the flow of polymers. To make sure that the development of a large deformation (up to 100% under compression) is caused by the flow rather than deep destruction of the polymer, it is necessary to make a parallel thermogravimetric analysis (to obtain a thermogravimetric curve). The ego is especially important in the case of heat-resistant polymers for which the development of large deformation occurs in the temperature range of 600-800 ° C, and this deformation caused by deep thermal destruction of the polymer can be mistaken for flow. It should also be taken into account that in the process of thermomechanical tests, in addition to the destruction, structuring can occur. These two processes always co-exist when the polymer is heated, but one of them proceeds at a much higher rate and determines the direction of the whole process. Structuring can manifest itself in the formation of transverse bonds between polymer chains, cyclization, etc. As a result, the beginning of the polymer flow will be suspended, and on the thermomechanical curve, a platform similar in form will appear in the area of high elasticity for linear polymers.

The temperature of the onset of intense thermal destruction of polymers 223

Thus, when analyzing the influence of the chemical structure on the thermal degradation of the polymer, it is possible to scan at various polar points, both at the ends of the filament I, hak, and in repeating units. In this case, it may turn out that the decomposition temperature of these filters is lower than the temperature at the onset of intensive thermal degradation of the polymer as a whole. Further scanning is desirable, taking into account the chemical transformations that occur during polymer spinning. Naturally, such a calculation can not completely replace the experimental studies.

Between the initial state of polymerization and the destruction of the zeros, lcra, there is a direct relationship; for example, in the thermal destruction of polymers having a low value of the heat of polymerization, a monomer is mainly formed, i.e., a depolymerization process takes place if the polymer contains secondary and tertiary carbon atoms and has a high value of the heats of polymerization, while under the thermal destruction, the monomer is almost not formed, and the process leads to the formation of stable low molecular weight macromolecules. To slow down the depolymerization reaction, a copolymerization method is used with a monomer that is prone to chain reaction upon degradation. Thus, a copolymer of methyl methacrylate a with acrylonitrile (a small amount) is less prone to a depolymerization reaction than polymethylmethacrylate because of the stability of the radical - CH-C-, formed in cesium.

The above reasoning iodrazu.meet constancy of flow. It should be noted that through. A temperature increase in temperature is undesirable not only from the position of the hydrodynamic conditions of operation, which the author speaks about, but also because of the possible thermal destruction of polymers, which significantly reduces the physicommechanical properties of the products obtained. - При.ч. Ed.

Thus, the thermal decomposition (or pyrolysis) of polymers can begin at the end of the macromolecule (depolymerization) or from its middle (decay according to the law of the case). To prevent polymer breakdown, it is necessary to block the ends of macromolecules. Decay according to the law of chance is impossible to prevent, since it is determined only by binding energies in the molecule, however, by binding free radicals to inhibitors of free radical reactions, it seems possible to slow down the process of thermal destruction of the polymer.

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