Aromatic polymers obtained by precipitation polycondensation. 6. Morphology of polyketone particles.

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ABSTRACT

Syntheses of aromatic polyketones in the form of particles, were performed using a very small monomer concentration (0.05 mol/L) by the precipitation polycondensation method. Some of these particles present highly ordered elongated needle-like structures (whiskers) particularly for the all-para polyketone samples. The use of isophthaloyl instead of terephthaloyl, for the same low monomer concentration produces, in addition to the globular particles bundles of ribbon-like structures. The average size of the needle-like particles is of 1-5 μm in width and of 150-250 μm in length. The factors controlling the morphology texture and size of the whiskers and ribbons are shown to be the polymer structure and the reaction conditions. Formation mechanisms are discussed.

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INTRODUCTION

It is well known that the properties of organic high molecular weight compounds are determined by chemical structure and morphology. Depending on the processing conditions, polymers with the same chemical structure may show widely varying morphologies, from completely disordered (amorphous) to highly ordered structures. In many cases, due to the close packing of polymer chains, highly ordered structures may show improved performance in comparison to isotropic systems. From this point of view, the investigation of highly ordered polymer structures provides a valuable information for detailed structure-property correlations.

Highly ordered polymer structures can be obtained by means of a variety of methods. Thus, precipitation from dilute solutions gives rise to well defined chain folded single crystals with sizes of up to several μm for many polymers [1,2]. On the other hand, crystallization during polymerization often results in larger single crystals with little chain folding and few internal defects [3].

Needle-like extended chain polymer crystals (whiskers) with an aspect ratio of at least 10:1, were prepared by solid-state polymerization of monomer single crystals [4-6]. In 1976 Economy and coworkers reported the synthesis of poly(oxy-1,4-phenylene-carbonyl) from acetoxybenzoic acid in a mixture of ortho-, meta- and para-isomers of cyclohexylbiphenyls and dicyclohexylbiphenyls at 300-320°C and the unexpected isolation of single crystals formed during polycondensation [7]. This work accelerated research in the preparation of chain extended crystals, and many studies have been conducted in this area [8-15]. However, these studies have shown that only a few polyesters, such as poly(4-hydroxybenzoic acid), poly(6-hydroxynaphthoic acid), poly[N-(4-carboxyphenyl)-4-hydroxyphthalimide], poly(4'-hydroxybiphenyl-4-carboxylic acid) are capable of forming whisker-like crystals in the course of high temperature solution polycondensation [15]. It should be noted that copolymerization (e.g., p-acetoxybenzoic acid and m-acetoxybenzoic acid) hinders the formation of polymer crystals due to the low capability of the polymer chains to crystallize [16]. Apart from that, the crystal growth of whiskers appeared to be highly sensitive to the presence of impurities or reaction by-products [15].

Highly ordered structures (e.g., lamellar single crystals, single disclination domains, etc.) of many aromatic polymers have been obtained by crystallization during high temperature melt polycondensation conducted between two glass slides [17]. This method, called "confined thin film melt polymerization" (CTFMP) was used for the preparation of polyesters, polyamides, polybenzamides and polyimides [17].

One important class of polymers among engineering thermoplastic resins, which are in growing demand, at the present time, are aromatic polyketones [18-20]. In preceding studies [21-24] we have shown that polyketones can be successfully prepared by precipitation polycondensation

at low temperature.

The aim of this work is to describe the development of the morphology of highly ordered structures "whiskers" during the synthesis of aromatic poly(ether ketone)s, using very low monomer concentrations. The influence of monomer structure (meta and para substituted phenylene) on the particle morphology is highlighted.

EXPERIMENTAL

Materials

1,2-Dichloroethane, isophthaloyl chloride and terephthaloyl chloride, all from Aldrich, were distilled prior to use. Aluminium chloride was sublimed prior to use. Diphenoxybenzophenone was obtained according to the previously published method [23].

Polycondensation

The polyketone samples were prepared as follows: a 300-ml, three-neck flask equipped with a magnetic stirrer, nitrogen inlet, thermometer, solids addition funnel, gas outlet, was purged with dry nitrogen and charged with 1.832 g of diphenoxybenzophenone, (0.005 mol), 1.015 g of terephthaloyl chloride (0.005 mol) and 100 ml of 1,2-dichloroethane. The addition funnel was charged with 2.58 g of high purity AlCl_3 (0.0194 mol). The transparent, colourless solution was cooled to -15°C , aluminium chloride was added to the solution and the reaction mixture was stirred for 30 min. Thereafter, the temperature was raised to 20°C over 2 h, and the reaction was continued at this temperature for 20 h. The suspension obtained was finally filtered. The precipitate was washed with methanol, extracted with boiling methanol for 20 h, and allowed to dry in air. The air-dried product was heated at 100°C overnight under vacuum to give 2.42 g of the polyketone **1** (97.2 % yield). The inherent viscosity (2.18 dLg^{-1}) was measured from polymer solutions in 94.5 % sulfuric acid at 25°C in a viscometer of the Ubbelohde type.

For the preparation of polyketone **2** 1.832 g of diphenoxybenzophenone, (0.005 mol), and 1.015 g of isophthaloyl chloride were used. Polycondensation was conducted in a similar manner and a polymer with an inherent viscosity value of 3.31 dLg^{-1} and a yield of 94 % was obtained.

The schematic chemical formula of polyketone **1** and **2** is:

Techniques

The morphological studies were conducted using an ISI DS-130 scanning electron microscope (SEM) coupled to a Be-window Kevex Si/Li detector and a Sparcstation 5 for image processing and X-ray dispersive energy analysis. To prevent the accumulation of static charge the samples were sputter-coated with a thin film of Au/Pd alloy.

Other techniques such as ^1H NMR spectroscopy, thermogravimetry (TGA) and differential scanning calorimetry (DSC) were used for a characterization of the products in a way similar to that previously reported [25-27].

RESULTS AND DISCUSSION

Synthesis

Preparation of poly(ether ketone)s by two different approaches has been described in the literature [17-19]. The first approach is a synthesis involving nucleophilic aromatic substitution [18-20], in which an aryl ether linkage is obtained:

where Ar, Hal and M denote the aromatic group, the halogen and the metal atoms, respectively.

The second approach involves an electrophilic aromatic substitution, in which an aryl ketone linkage is formed:

We have recently shown [21,22] that precipitation electrophilic Friedel-Crafts polycondensation can be performed in such a way that the polymer precipitate presents quite uniform small particles. We used this method for the preparation of aromatic polyketones [23-26].

Thus, electrophilic polycondensation of terephthaloyl (or isophthaloyl) chloride with diphenoxybenzophenone in the presence of AlCl_3 proceeds as a typical Friedel-Crafts polyacylation, with elimination of hydrogen chloride as a by-product. In the course of the synthesis, the polymer/catalyst complex begins to precipitate from the reaction medium. However, the polymer

forming reaction also continues in the precipitate. Unambiguous evidence for this process has been obtained recently [25].

It is to be noted that isolated particles are obtained at low monomer concentration [26]. High monomer concentrations result in massive polymer aggregates with low viscosity. The effect of monomer concentration was also observed during preparation of polyester whiskers [11, 14].

After completion of the reaction, the particles formed are isolated from the reaction medium by filtration. Pure polyketone particles are recovered by washing with methanol and acetone, followed by drying.

Particle Morphology

a) Polyketone 1

We have previously reported the influence of monomer concentration on polymer structure and morphology of polyketone particles [26]. For the smallest concentration used (0.083 mol/L) spherical particles together needle-like structures were observed. In the present study we have decreased the monomer concentration used (0.05 mol/L) in order to improve the amount and quality of needle-like particles. Indeed, we have observed longer needle-like particles but in a similar relative amount to the spherical particles than previously reported [26].

In the case of polyketones 1 (all para-substituted phenylene) the particles 200–600 μm in size (Fig 1a) are aggregates of many smaller particles (Fig 1b). Higher magnification (Fig 1c) reveals the presence of many spherical and needle-like particles. Some of the needle-like particles have a length of 150–250 μm and a width of 1–5 μm . Even higher magnifications (Fig 2) show that the needle-like particles have different geometrical cross-sections, e.g., triangles, rectangles, etc.

In our previous work [27] it was shown that these polyketone 1 materials show 2 polymorphic forms. Form II which has been found in the material as obtained, showing only globular particles. Upon prolonged thermal treatment Form II converts into the more stable crystal Form I. In order to correlate the crystalline phases to the two appearing morphologies we have carried out X-ray diffraction experiments on the sintered material before (bottom) and after (top) annealing treatment at 230°C for 15 minutes (Fig 3). Although the sintered untreated sample shows a very low crystallinity one can, nevertheless, recognize some weak reflections which can be attributed to the polymorphic form I [27]. We attribute these reflections to the needle-like particles which are the minor component. After the short thermal treatment used a substantial amount of material crystallizes showing the typical diffractogram of Form II. Thus, the diffractogram in Fig 3 (top) shows the superposition of both phases corresponding to the needleless (Form I) and to the globular particles (Form II) The relative amount of whiskers to globular particles in the sample can be estimated to be 5–10%.

A preliminary study of electron diffraction (at 76 kV) from individual needle particles reveals the appearance of spot reflections [28]. Therefore, one may speculate that the needles are extended chain crystals (whiskers). This will be confirmed when real time X-ray scattering experiments of needles and ribbons using a microfocus are completed. Infrared dichroism of these needle-like particles (Fig. 4) reveal that polyketone chains are parallelly aligned to the direction of longest particle size [27].

Since the carbonyl groups of the reactants and the reaction products are complexed with AlCl_3 , the optimum ratio of AlCl_3 to $-\text{COCl}$ group was reported to be 1.35-1.45 [23-25]. Furthermore, if a co-monomer containing other carbonyl groups is used, (i.e., diphenoxybenzophenone), an additional amount of Lewis acid is required. As a result, a significant amount of AlCl_3 is present in the reaction medium during the synthesis. Therefore, the first question which arises concerns the origin of the needle-like particles: are they really organic materials?

The simplest way to prove this could be by elemental analysis. However, attempts to separate efficiently the needle-like particles from the rest of the material failed so far. Elemental analysis of the samples obtained shows the amount of aluminium in the materials to be less than 50 ppm. Therefore, it seems very unlikely that the needles are built up from inorganic material. Additional treatment of the samples with solvents by means of continuous extraction reduces the amount of residual catalyst to just a few ppm. (It should be noted that washing and further extraction of the particles does not change their morphology). Since direct local analysis of the needle-like particles by EDX does not reveal presence of the aluminium, we can conclude, therefore, that the needles are made of organic polyketones.

Because, the polymers obtained are soluble in sulfuric acid and in a $\text{CF}_3\text{COOH}/\text{CHCl}_3$ mixture, we could characterize them by viscosity and NMR measurements. The observed ^1H NMR spectrum of the polymer **1** is identical to that reported [26] corresponding to a polymer with para-substituted diphenyl ether fragments in the main chain.

As far as thermal properties are concerned, the 1st and 2nd DSC curves of the polyketone **1** show single melting peaks at 391°C and 352°C, respectively. These values are larger than those previously reported (about 385 and 342°C for sample P3) [27]. The larger melting temperatures observed for polymer **1** suggest the occurrence of larger sizes and perfection of microcrystals. This is presumably related to the more dilute monomer concentration used.

b) Polyketone 2

As mentioned above, in high-temperature solution polycondensation only a few polyesters are capable of forming whisker-crystals [15]. For linear para-substituted aromatic polyesters, incorporation of meta-substituted units in the main chain was shown to prevent the formation of polymer crystals [16].

In the present study, polyketones with meta-substituted units in the main chain (polyke-

tones **2**) have been also prepared using the same low monomer concentration as polyketone **1**. It is remarkable that these polymers, containing meta-substituted fragments, are found to present highly-ordered structures as well. The morphology of these structures is, however, quite different to that of the para-substituted polyketone. In this case they appear with a ribbon-like morphology nucleated at centers of radiating growth (Fig. 5a). These heterogeneous complex aggregates show many ribbons, developing, perhaps, from seemingly single nuclei. (Fig. 5b).

Occasionally, we have observed parallel aligned microfibrils coming out of the ends of prismatic particle (Fig. 6a,b). The presence of ribbon like particles instead of needle particles in the polyketone **2** ought to be related to the meta-substituted phenylene units which confer a non straight linear conformation to the polyketone chains. As a consequence the chains of polyketone **2**, although can form ordered morphologies (ribbons), they cannot offer particles with crystal habit (whiskers) as those observed for polyketone **1**.

CONCLUSIONS

On the whole, the preparation of various polyketones containing highly ordered structures is of specific interest from two points of view: firstly, it offers a possibility for the detailed analysis of the formation mechanism, structure and properties of new highly ordered polymeric materials; secondly, the polyketones obtained can be considered as composite materials, containing rigid reinforcement component (whiskers) in a matrix of globular particles. It is important that the reinforcement component has the same chemical composition as the matrix in which it is highly dispersed. The underlying concept is that the molecular reinforcement of a flexible chain-polymer with a rigid-rod structure would yield a class of materials with superior mechanical properties than those of the just pure compounds [29]. In addition, the composite is prepared "in situ" by a simple method.

For the first time it has been shown that these polyketone syntheses are accompanied by the formation of highly-ordered structures. The shape and size of the structures depends on polymer structure and reaction conditions.

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Figure Captions

- Fig. 1 Scanning electron micrographs of aggregates of polyketone **1** at different magnification (see text).
- Fig. 2 Morphology of needle-like particles of polyketone **1** at high magnification.
- Fig. 3 WAXD diffractograms for a sintered polyketone **1** sample before (bottom) and after (top) annealing at 230°C for 15 min.
- Fig. 4 Polarized infrared spectra of a single needle-like particle (from Ref 27): (dotted line) $\parallel$; solid line $\perp$.
- Fig. 5 Morphology of polyketone **2** showing ribbon-like particles and spherical particles at two different magnifications.
- Fig. 6 Morphology of polyketone **2** prismatic particles (a), showing a fibrillar structure (b).

a

b

c

Fig 1

Fig 2.

Fig. 3

~~Fig. 3~~
Fig. 4

Fig 4
Fig 5

a

b

Fig. 5

Fig. 6