SYNTHESIS of POLY(1,4-PHENYLENE-OXY-1,4-PHENYLENE-CARBONYL-1,3-PHENYLENE-CARBONYL)S (m-PEKK) by PRECIPITATION POLYCONDENSATION

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ABSTRACT

High molecular weight m-substituted poly(ether ketone-ketone) has been synthesized by electrophilic precipitation polycondensation via two different ways: reaction of isophthaloyl chloride with diphenyl ether and reaction of isophthaloyl chloride with 1,3-bis(4-phenoxybenzoyl)benzene. The second way of synthesis was found to give structurally more perfect polymers with higher molecular weights. In both cases polycondensation proceeded with precipitation of the polymers formed as uniform particles. The influence of reaction conditions has been studied. Monomer concentration and monomer stoichiometric ratio were shown to affect the polymer properties.

INTRODUCTION

Poly(ether ketone)s comprise class of polymers in which arylene groups are linked by ether or carbonyl groups [1,2]. These materials are a desirable class of polymers which are attracting increasing interest at the present time because of their high temperature stability and mechanical strength. Polyketones are, in addition, semicrystalline and, therefore, resistant to attack by solvents. While crystallinity gives the poly(ether ketone)s a unique set of enhanced properties among thermoplastics, it is this property, coupled with melting points generally above 320°C, which makes their synthesis so difficult. The preparation of poly(ether ketone)s by two different approaches has been described in the literature [1]. The first approach is an electrophilic synthesis in which an aryl ketone linkage is formed. The second approach is a nucleophilic synthesis in which an aryl ether linkage is obtained. The problem is how to keep the polymer in solution and so obtain high molecular weight polymers. The insolubility of these polymers presents a major synthetic problem as it limits the molecular weight that can be obtained before the growing chains crystallize out from the polycondensation system. This is why nucleophilic synthesis is conducted at 300°C and even higher, using solvents like diphenylsulfone. In electrophilic reaction, good results can be achieved by working in strongly acidic medium (i.e., system HF-BF_3), or in a mixture composed of a large excess of AlCl_3 as a catalyst, a Lewis base such as dimethylformamid or lithium chloride, and a chlorinated organic solvent such as methylene chloride or dichloroethane. Under these

The poly(1,4-phenylene-oxy-phenylene-carbonyl-1,3-phenylene-carbonyl) can be prepared by two different routes:

RESULTS and DISCUSSION

Precipitation polycondensation was conducted according to above mentioned method [6]. The viscosity of polymer solutions in 94,5 % sulfuric acid were measured at 25°C in a viscosimeter of the Ubbelohde type. The intrinsic viscosity was calculated by extrapolating reduced viscosity for zero concentration. The ^1H and ^{13}C NMR spectra of polymer solutions in $\text{CF}_3\text{COOH}-\text{CDCl}_3$ mixture were recorded on a Bruker AMX-600 spectrometer (600 MHz).

METHODS

1,2-Dichloroethane, isophthaloyl chloride (IPC) and diphenyl ether (DPE), all from Aldrich, were distilled prior to use. Aluminium chloride was sublimed prior use.

MATERIALS

conditions the polymer can be maintained in solution (or, to be more precise, in a reactive gel state). It is accepted that premature polymer precipitation from initially homogeneous solution in polycondensation synthesis prevents further macromolecular chain growth reactions. However, it has been mentioned [3,4] that polymer forming reactions can occur in precipitate; i.e., after phase separation. Recently we have shown [5]-[7] that electrophilic precipitation polycondensation can be performed in such a way that polymer precipitate presents quite uniform small particles. This process has unquestionable technological advantages since pure polymer can be recovered just by filtration followed by washing with organic solvents and drying. The application of this method for the preparation of both advanced and usual polymers is very promising. The aim of the present paper is to describe the preparation of aromatic meta-substituted poly(ether ketone)s by the electrophilic precipitation polycondensation method. The polymers have the following chemical composition:

One may to assume that comparison of results of the syntheses performed by these two routes will be helpful for a better understanding of the precipitation polycondensation method.

All the syntheses were carried out in the same manner: reaction of isophthaloyl chloride with diphenyl ether and with 1,3-bis(4-phenoxybenzoyl)benzene, conducted in 1,2-dichloroethane, in presence of a Lewis type catalyst, such as anhydrous aluminum chloride, proceeded as a typical Friedel-Crafts polyacylation involving dicarboxylic acid chloride and aromatic hydrocarbons, with elimination of hydrogen chloride as a byproduct. Because the carbonyl groups of the reactants and the reaction products are complexed with $AlCl_3$, and thereby deactivate it, the $AlCl_3$ is generally employed in the amount of more than one equivalent of carbonyl groups in the reaction medium. Furthermore, if comonomer containing other carbonyl groups is used, (i.e., 1,3-bis(4-phenoxybenzoyl)benzene in polycondensations by second route), an additional amount of Lewis acid will be required.

Despite of the large structural difference between diphenyl ether and 1,3-bis(4-phenoxybenzoyl)benzene, polycondensations involving these monomers preceded in quite similar manner.

Figure 1. Dependence of the polymer viscosity on reaction time in polycondensation of isophthaloyl chloride with diphenyl ether: (O) precipitated polymer, (●) polymer in the solution.

The preparation of the polyketones generally starts at lower temperature. A colored, homogeneous solution is formed when catalyst is added at low temperature to the monomer mixture dispersed in the solvent. The initial low temperature is

needed to maintain control over the reaction rate. Reaction temperature of about -15°C to 0°C has been found to be particularly effective.

In the course of polymer synthesis the polymer/catalyst complex begins to precipitate from the reaction medium (Fig.1). Because of the relatively low monomer concentration, the precipitate appears in the form of swollen, isolated particles. After completion of the reaction, the particles formed are isolated from reaction medium by filtration. Pure polyketone particles are recovered by washing with methanol and acetone followed by drying. The washed and dried polymer particles of 0.1-0.5 mm in size, are smooth and glass-like, with many spheric ones among them. The particles are completely soluble in sulfuric acid and $\text{CF}_3\text{COOH-CDCl}_3$ mixture. The satisfactory solubility of the synthesized polyketones allowed us to characterize them by viscosity and NMR measurements.

Polymer precipitation usually begins at early stages of the synthesis. Thus, in polycondensation of isophthaloyl chloride with diphenyl ether the precipitation occurs in the first 40-60 min. From Fig.1 one sees that during the first hour viscosities of the polymer in precipitate and the polymer which still remains in solution are rather close. However, for increasing reaction times viscosity of the polymer in the precipitate increases, while the viscosity of the polymer in solution remains practically constant. Simultaneously, the amount of polymer in solution decreases owing to the increasing amount of precipitate (Fig.2).

Figure 2. Dependence of polymer yield on the reaction time: (O) precipitated polymer, (●) polymer in the solution.

Analysis of the data of Fig. 1 unambiguously points to the presence of macromolecular chain growth reactions in the precipitate. The amount of the latter is increased

during polycondensation. It should be noted, that viscosity (molecular weight) of the polymers is quite high. One may assume that the high molecular weight is due to the high local concentration of active end groups in the particles. Consequently, each particle can be considered as a reactor.

In a polycondensation reaction the polymer properties are significantly influenced by the monomer concentration. Fig. 3 shows the influence of the monomer concentration on the polymer viscosity in the precipitate and in solution, respectively.

Figure 3. Dependence of polymer viscosity on monomers concentrations: (O) polycondensation of IPC with DPE, (●) polycondensation of IPC with BPBB.

For both polycondensation routes used maximum viscosity values were obtained for the same monomer concentration range (0.05-0.1 mol/l). The viscosities of the polyketone based on isophthaloyl chloride and 1,3-bis(4-phenoxybenzoyl)benzene are significantly higher. It should be mentioned that the sharp viscosity peaks in that range show very good reproducibility. For monomer concentrations higher than 0.4-0.6 mol/l large macroscopic aggregates are formed instead of uniform particles.

In classical polycondensation of two monomers the molecular weight of the polymer formed is strongly dependent on monomer stoichiometric ratio. The excess of one of two monomers usually results in a dramatical decrease of molecular weight. Therefore, the dependence is very important for the precipitation polycondensation where phase separation can result in stoichiometric disbalance.

However, the dependence of viscosity on monomer ratio in the case of polycondensation of isophthaloyl chloride with diphenyl ether (Fig. 4) shows surprisingly "classical" pattern, with maximum viscosity values corresponding to 1:1 monomer

ratio. It is noteworthy that an increasing of the monomer disbalance causes a slow reduction of the polymer viscosity. For example, even at 5% mol. excess of diphenyl ether it is possible to obtain high viscosity polymers. On the other hand, an excess of diphenyl ether in that case leads to polymers with stable end groups. After extraction with methanol and acetone the polyketone particles consist of about 50 ppm of aluminium. Additional treatment of particles with solvents by means of continuous extraction reduces the amount of catalyst residue to a few ppm. It is to be noted that washing and extraction of the particles did not change their shape.

Figure 4. Dependence of the polymer viscosity on monomer stoichiometric ratio in polycondensation of IPC with DPE: (●) excess of IPC, (○) excess of DPE.

The structure of the polymers was characterized by NMR spectroscopy. In the ^{13}C NMR spectra of polyketones prepared by different ways the signals can be completely accounted for polymers with para-substituted diphenyl ether fragments in the main chain. However, the more sensitive ^1H NMR spectra of these two polyketones solutions (Fig. 5), show, besides those main signals corresponding to the expected structure, some additional smaller signals, which can come from defect structures. For example, in the spectrum of polyketone prepared by first way weak signals at 4.0, 8.05-8.10, 8.18, 8.24, 8.5 and 8.65 ppm are observed. It is worthy to mention that the amount of these signals (defect structures) is significantly less for polyketone, prepared by second way. Therefore, regioselectivity in the condensation of IPC with BPBB is much higher than in condensation of IPC with DPE. (The observed splitting of doublet at 8.13 ppm in the spectrum of the polyketone based on IPC and BPBB is due to interaction of H_f protons with H_e proton.)

D.S.C. traces of the polyketones obtained by two ways revealed practically the same melting points at 263°C, although there are some differences in the shape of the curves.

CONCLUSIONS

The meta-substituted poly(ether ketone) was prepared via two different ways: by reaction of electrophilic substitution of isophthaloyl chloride with diphenyl ether and by reaction of isophthaloyl chloride with 1,3-bis(phenoxymethyl)benzene. The polymer syntheses were performed through precipitation polycondensations, and polyketones were obtained in form of particles. The second route leads to structurally more perfect polymers with higher molecular weight. Polyketones, obtained by the two different routes, showed similar melting points. On the whole, preparations of the polyketone by both ways allows to optimize the synthesis conditions and to obtain linear high molecular weight polymers in particle form.

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