

SYNTHESIS OF PERFLUOROPOLYETHER LUBRICANT

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Introduction

The perfluoropolyether (PFPE) is a well known class of fluids useful as lubricants for high technology applications due to their excellent physical and chemical properties. They are strategic for nuclear, aerospace and electronic industries, thus, it was decided to develop the synthesis of some special grades for high vacuum purpose. Perfluoropolyether synthesis involves complex steps from monomer production to the characterization of final product.

The thermal decomposition of chlorodifluoromethane (R-22)⁽¹⁻⁵⁾ and tetrafluoroethene (TFE)⁽⁶⁻⁸⁾ to obtain TFE and hexafluoropropene (HFP), respectively, may be considered as the first stages of a most complex process leading to the synthesis of the PFPE. These monomers were obtained with a 99% purity. After monomers synthesis HFP photo-oxidation and polymerization was carried out at low temperature⁽⁹⁾. The reaction was activated through ultraviolet radiation by a medium pressure mercury lamp. It was obtained an acid perfluoropolyether, which was distilled. The distillation of this product followed ASTM-D1160/87 standard used by Sianesi et al.⁽⁹⁾, providing cuts of increasing viscosity. The high molecular weight cuts were degraded using $AlCl_3$ as catalyst which it has been studied before by Viola et al.⁽¹⁰⁾.

The fluorination process was selected for acid end groups capping. Fluorination was carried out passing a flow of fluorine diluted with an inert gas into a liquid phase of PFPE, following Sianesi method⁽¹¹⁾. The reaction was conducted up to the completeness or at least, to a satisfactory disappearance of original acids terminal groups.

In this work, it was studied the various important steps for the PFPE synthesis, according to:

- monomer tetrafluoroethene production;

- monomer hexafluoropropene production;
- hexafluoropropene photo-oxidation and polymerization;
- distillation and degradation of perfluoropolyether;
- perfluoropolyether fluorination;
- characterization of intermediates and final products.

It is presented a review of the main features for each process and the results regarding yield and purity.

It was produced PFPE 06/6 grade with a 10% yield from monomers production.

Experimental Procedure

The perfluoropolyether synthesis was initiated by monomer production. The monomer tetrafluoroethylene was obtained by chlorodifluoromethane (R-22) pyrolysis. The R-22 was pyrolyzed in platine tube of 2.2 mm inner diameter and 1250 mm length, 950°C temperature, 0.05 s contact time and 1.2 kgf/cm² pressure. The pyrolysis products were purified by a distillation column at low temperature. In this way, it was possible to obtain pure TFE. The HFP was produced by TFE pyrolysis. It was used a stainless steel tubular reactor with 3.6 mm inner diameter and 490 mm length, 960°C temperature, 0.13 s contact time and 1.2 kgf/cm² pressure. The reaction mixture was purified through a distillation column obtaining pure HFP. The pyrolysis reaction and the purity of the monomers (TFE and HFP) were accomplished by gas chromatography. The chromatographic analyses were carried out in a gas chromatograph model CG-500A with Porapak Q column, thermal conductivity detector and hydrogen carrier gas.

The pure HFP was employed for photo-oxidation and polymerization. It was employed the experimental procedure proposed by Sianesi et al.⁽⁹⁾ with minor changes. Basically, the main parts of polymerization system were: the polymerization reactor with a reflux condenser; the ultraviolet source with cooling system; washing neutralization and drying columns for O₂ purification; the O₂ gasometer and the system for storage of new and used HFP. It was employed as ultraviolet source, a medium pressure Hg vapor lamp, Hanau T-150. The polymerization reaction was performed at -70°C. Oxygen was continuously supplied to the polymerization medium. After 48 hours reaction, the mixture HFP+O₂ was converted to the raw PFPE. Thus, the raw polymer was subjected to distillation and fluorination.

The distillation of this product, attended the ASTM D-1160-87. It was carried out at 0.3-0.4 Torr and temperature up to 350°C, providing standard cuts of increasing viscosity. The distillation of the perfluoropolyether acid yielded several fractions, which molecular weight distributions was determined.

The number average molecular weight of each cut was obtained from the viscosity measured at 20°C, using the following equation:

$$\eta = 5.3 \cdot 10^{-7} \cdot MW^{2.474}$$

where: η = viscosity at 20°C

MW = number average molecular weight

The degradation studies were performed using the cuts with higher molecular weight than the useful ones. It was used a flask connected to a condenser. The AlCl_3 (1%) was used as a catalyst. The PFPE dispersion/ AlCl_3 was mixed and heated to 250°C for about 1 hour.

After the distillation and degradation, the PFPE cuts were neutralized by means of direct fluorination. Capping reactions were performed using a commercial fluorine/nitrogen gas cylinder from Air Products Company. Fluorination was carried out in a glass reactor with 1000 ml capacity where the stirred polyether was heated (from 100°C to 270°C) while bubbling a slight excess of fluorine. Under these conditions, the reactions were completed at approximately 24 hours. After that, oil viscosity was evaluated and the infrared spectrum was obtained to check the neutralization of the PFPE.

Results and Discussion

The TFE and HFP monomers were obtained with a purity higher than 99.9% as verified by CG/TCD. R-22 conversion was 69% and TFE yield, 94% for TFE production. TFE conversion was 35% and HFP yield, 90%. These results are in accordance with the best ones found in the literature^(5,8).

In HFP photo-oxidation and polymerization, it was obtained a transparent product having a strong acid and a viscous character. The infrared spectra was similar to Sianesi's one⁽⁹⁾. It showed absorption bands at 1897 cm^{-1} and 1781 cm^{-1} due to the presence of -COF and -COOH end groups, respectively. The -COOH end group was eventually created by the hydrolysis of -COF end group.

Raw PFPE was distilled obtaining cuts in a range of molecular weight from 1000 to 5000 u. Figure 1 shows the molecular weight distribution of the raw PFPE. In order to achieve the 06/6 grade, cuts in the range of molecular weight from 1000 to 3000 u were blended in suitable amounts. It was done a balance between the viscosity of each cut and its volume to fit properly the grade viscosity and vapour pressure. Figure 2 shows the molecular weight distribution of 06/6 grade, the most important one in this work. These results are in accordance with Caporiccio's⁽¹²⁾ one.

The heavier cuts, from 3000 to 5000 u, were thermally degraded to improve the yield for grades with commercial interest. It was obtained the 25/05 grade.

Then, acid polymer was subjected to fluorination up to complete neutralization. After fluorination, the infrared spectrum didn't show the absorption bands in 1897 cm^{-1} and 1781 cm^{-1} regions relative to the -COF and -COOH groups. Thus, according to infrared sensitivity, the neutralization was achieved.

It was verified that 1000 g of R-22 was necessary to synthesize 108 g of 06/6 and 43 g of 25/05 grades corresponding to a 10% and 4% yields, respectively. So, after all these steps, it was obtained a PFPE oil completely characterized, equivalent to the 06/6 grade, ready to be used in various industrial applications.

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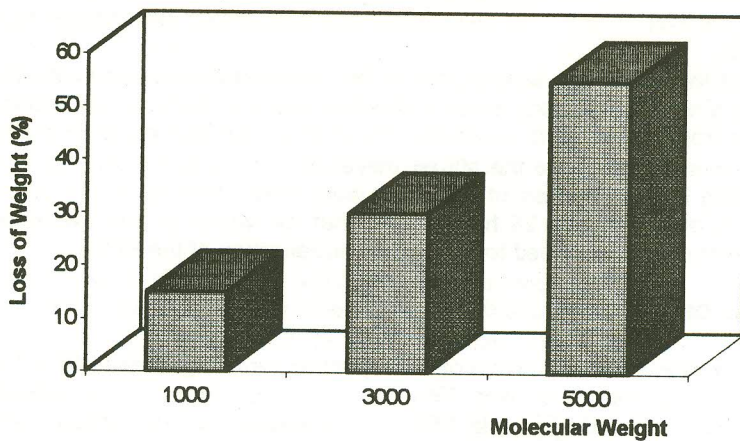


Figure 1. Molecular Weight Distribution of Raw PFPE

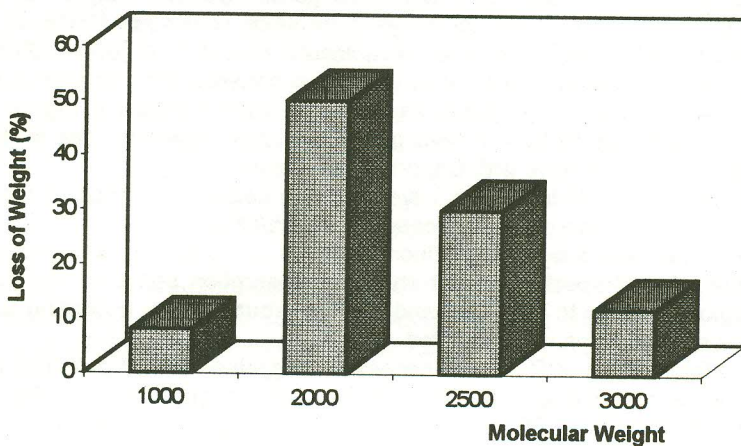


Figure 2. Molecular Weight Distribution of 6/06 Grade

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