

## Investigation of the dispersion process of polypropylene glycol in perfluorodecalin

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**Abstract:** Perfluorinated polyesters (PFPE) are used as components of high-performance lubricants and oils operating in high and low temperature conditions, including in special-purpose products used in space and in Arctic conditions. To date, the methods for producing PFPE are complex processes that are quite demanding to the conditions of synthesis, which makes it almost impossible to produce these compounds commercially on a large scale. One of the promising approaches to obtaining perfluorinated esters is liquid-phase direct fluorination. Toxic, ozone-depleting solvents have been used in these processes. When they are replaced with harmless, perfluorinated liquids, for example, perfluorodecalin (PFD), another problem is found – the original polyesters are insoluble in PFD, which is confirmed by laser microinterferometry. In this regard, ultrasonic dispersion of the initial polypropylene glycols (PPGs) of various molecular weights in PFD was proposed in order to obtain emulsions for subsequent direct fluorination. The resulting emulsions were studied using gel-penetrating chromatography, dynamic light scattering and gravimetry. According to the results of the study, the values of particle sizes and emulsion concentrations were obtained over time after ultrasound, and it was also concluded that the stability of the molecular weight of PPG in the emulsion after sonification. The applicability of ultrasonic dispersion for a high specific surface area of the phase boundary in the PPG – PFD system is discussed, and the feasibility of sonification in a continuous or batch mode when implementing liquid-phase fluorination of PPG in PFD is also discussed.

**Keywords:** polypropylene glycol; perfluorodecalin; emulsion; ultrasonic dispersion.

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## Исследование диспергирования полипропиленгликоля в перфтордекалине

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**Аннотация:** Перфторированные полиэфиры (ПФПЭ) находят применение в качестве компонентов высокоэффективных смазок и масел, работающих в условиях высокой и низкой температуры, в том числе в изделиях специального назначения, используемых в космосе и арктических условиях. Существующие коммерчески доступные ПФПЭ являются продуктами мономерного синтеза, что неизбежно приводит к неоднородной структуре конечного продукта. В связи с этим, исследование новых подходов получения изотактических ПФПЭ – актуальная задача. Одним из перспективных подходов к получению изотактических ПФПЭ является жидкофазное фторирование. На сегодняшний день в жидкофазном фторировании применяют

токсичные, озоноразрушающие растворители, что ограничивает промышленную реализацию. Использование перфторированных жидкостей, например перфтордекалина (ПФД), позволит снизить экологические риски синтеза ПФПЭ. Учитывая нерастворимость полипропиленгликолей (ППГ) в ПФД, предложено использование ультразвукового диспергирования для получения эмульсий и жидкофазного фторирования. Приведены исследования свойств эмульсий ППГ в ПФД, определены концентрация, средний размер частиц и молекулярно-массовое распределение. Сделан вывод о применимости ультразвукового диспергирования для обеспечения высокой удельной площади поверхности раздела фаз в системе ППГ–ПФД, а также целесообразности проведения ультразвукового диспергирования в непрерывном или периодическом режиме при реализации жидкофазного фторирования ППГ в ПФД.

**Ключевые слова:** полипропиленгликоль; перфтордекалин; эмульсия; ультразвуковое диспергирование.

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## 1. Introduction

Perfluorinated polyesters are widely used as oils and lubricants [1] for extreme temperatures. At the moment, two strategies for obtaining perfluorinated polymers are known: the monomeric route and direct fluorination. The monomeric route involves the polymerization of perfluorinated monomers. The disadvantages of this method are the complexity of controlling the structure and properties of the resulting products, the inevitability of the formation of residual peroxide groups [2], which, upon reduction, lead to a decrease in the molecular weight of oligomers.

Direct fluorination of commercially available polymers with gaseous fluorine was described in [3–8].

Liquid-phase fluorination provides a reduction in local heat release in exothermic processes and allows the process to be carried out at a higher speed. Liquid-phase fluorination is carried out by dissolving the starting material, or suspensions and emulsions are subjected to fluorination [9–12].

It was shown that liquid-phase fluorination of polypropylene glycols (PPG) proceeds without changing the carbon skeleton of the polymer [13], however, the use of expensive, toxic, ozone-depleting liquids as a liquid phase [14–16] limits industrial application.

Fluorination of polymers in a perfluorinated liquid, such as PFD, is a promising method for the preparation of fluorinated polymers [17–19] due to the high chemical stability of perfluorocarbons and the solubility of gases in them. It was shown in [17] that surface fluorination is accompanied by the dissolution of the fluorinated polymer in PFD; accordingly, the provision of a high interfacial surface significantly affects the rate of the process.

This paper is focused on the study of the properties of PPG emulsions in PFD with the aim of applicability for subsequent fluorination. In this

study, we show the compatibility of PPG and PFD, determine the patterns of using sonification to obtain an emulsion of PPG in PFD, the effect of sonification on the change in the molecular weight distribution of PPG with different molecular weights. The research results will make it possible to establish the feasibility and optimal parameters of fluorination of PPG in PFD to obtain perfluorinated ethers with a given molecular weight.

## 2. Materials and methods

### 2.1. Materials

In our study, we used PFD produced by LLC Khimzavod Fluorosalts with a basic substance content of 99.2 %; PPG with a molecular weight of 425, 2000, 4000 Da from Acros OrganicsTM (CAS: 25322-69-4); Chloroform of special purity grade for gel permeation chromatography (GPC) from the company “Galakhim”. The GPC system was calibrated using a set of InfinityLab EasiVial PEG/PEO standard samples (Agilent Technologies).

### 2.2. Methods

#### 2.2.1. Laser microinterferometry

To study the compatibility of PPG and PFD, laser microinterferometry was used [20]. A PPG sample was placed between translucent glasses, and a gap of 60  $\mu\text{m}$  was fixed with polyimide spacers. Then PFD was poured into diffusion cells. The moment of contact of the components was considered to be the beginning of the diffusion process. The measurements were carried out in the mode of stepwise increase and decrease in temperature from 20 to 120 °C. A KLM-A532-15-5 modular laser with a wavelength of 532 nm was used as a light source. Interference patterns were recorded using a digital video camera with image transfer to a computer.

In addition, the refractive indices of PPG and PFD at 25°C were determined using an IRF-22 refractometer. The difference between them was 0.13, which corresponded to the formation of 24–25 interference fringes in the interdiffusion zone.

### 2.2.2. Sonification method

The PPG dispersion was carried out on an ultrasonic disperser UZDN-0.3 manufactured by Kriamid LLC (Moscow, Russia), which consists of the following components: an ultrasonic generator GU-22-800 with a maximum power of 800 W with adjustable voltage pulses from 200 to 500 V and frequency from 22 to 23 kHz to adjust to the resonance of the system; an oscillatory system, which is an assembly of a water-cooled magnetostrictive transducer and a submersible waveguide made of titanium with a diameter of 5 mm.

Sample weights PPG and PFD in the required ratio were placed in a glass beaker with a volume of 50 ml, then the waveguide of the ultrasonic disperser was lowered 2–5 mm into the layer of initial reagents, the dispersant was turned on, and the frequency was adjusted to the resonance of the system for maximum cavitation in the reaction volume. The time of ultrasonic exposure was 3 minutes, in the case of experiments for GPC, it was 45 minutes.

### 2.2.3. Gravimetric method for determining of PPG emulsions in PFD concentration

To measure the concentration of PPG in the emulsion, a gravimetric method was used. The experimental data in Table 1 confirm that the PPG evaporation rate is 100–1000 times lower than the PFD evaporation rate at temperatures of 60–180 °C.

The essence of the method is to determine the mass of PPG in the emulsion, taking into account the fact that at a given temperature, all PFD evaporates, and all PPG remains in a condensed state.

**Table 1.** Evaporation rates of PPGs and PFD at different temperatures

Substance	Evaporation rates, mg·min <sup>-1</sup>		
	60 °C	120 °C	180 °C
PFD	210	247	492
PPG425	0.14	0.3	1
PPG2000	0.11	0.16	0.67
PPG4000	0.07	0.12	0.4

For this purpose, crucibles with emulsion weights of about 20 g were placed in a drying oven, which provided a stable temperature control mode ( $60 \pm 2$ ) °C. Mass measurements were carried out using an Acculab ALC-210d4 analytical balance with a resolution of 0.1 mg.

### 2.2.4. Particle size determination

A DelsaMax Pro particle size analyzer, Beckman Coulter, was used to evaluate the particle sizes of the emulsified PPG in the resulting emulsions. The measurements were carried out at a wavelength of 589 nm; the thermostat temperature of the measured cell was 21 °C. To average the result of the measurement, 10 measurements of dispersion were taken for 5 seconds each. Such measurements were repeated five times on one sample. At the end of dispersion, an aliquot was taken from the emulsion volume into a dry, cleaned polymer cuvette with a volume of 1.5 mL. For emulsions of PPG with a molecular weight of 425, 2000, 4000 Da in PFD, the average particle radius was measured after sonification after 1, 2, 3, and 24 hours.

### 2.2.5. Gel permeation chromatography

The LC-20 Prominence GPC system (Shimadzu, Japan) consists of a high-precision liquid pump LC-20 AD (Shimadzu, Japan), a DGU-203R Prominence degasser (Shimadzu, Japan), a CTO-20A/AC column furnace (Shimadzu, Japan), a refractive index detector RID-20A (Shimadzu, Japan) and an Agilent Technologies 7.5 × 300 mm column (PLgel 5 µm MIXED-C), providing an effective molar mass determination range from 200 to  $4 \times 10^5$  Da. The injection volume was 20 µL. Chloroform was used as the eluent at a flow rate of 1 mL·min<sup>-1</sup> at 40 °C.

The original PPG samples and standard samples were dissolved in chloroform before analysis. In the case of studying the molecular weight distribution (MWD) of PPG after sonification, PFD was first evaporated from the emulsion under vacuum at 60 °C, and the residue was dissolved in chloroform. Before analysis, all samples were filtered through PTFE filters with a pore size of 0.75 µm.

The weight average ( $M_w$ ) and number weight ( $M_n$ ) were evaluated using Shimadzu LC Solution software. The polydispersity index (PDI) was calculated as the ratio between  $M_w$  and  $M_n$ .

### 3. Results and discussions

#### 3.1. Compatibility of components in the PPG – PFD system

Typical interferograms of zones of mutual diffusion of the PPG – PFD system are shown in Fig. 1.

It can be seen that the interference fringes on both sides of the interface did not change at all temperatures and PPG molecular weights. There is no penetration of components into each other, i.e. PPG and PFD are mutually insoluble.

#### 3.2. The effect of sonification on the molecular weight distribution of PPG

Due to the insolubility of PPG in PFD, it was decided to investigate the process of emulsification of PPG in PFD using an ultrasonic disperser. It is known that sonification can lead to a change in the MWD of polymers [21, 22], which can critically change the structure and properties of the resulting product. In this regard, we studied the MWD of PPG by GPC before and after ultrasonic dispersion. It has been experimentally established that sonification of the PPG-PFD system for 3 minutes leads to a visually homogeneous emulsion throughout the volume. It is known that fluorination processes can take place over several hours, which indicates the potential need for periodic sonification to maintain a high specific surface area of the PPG – PFD interface. In this regard, to conduct GPC analysis, the time of ultrasonic exposure to the PPG – PFD system was increased 15 times. The values of  $M_w$ ,  $M_n$  and PDI are given in Table 2 and in Fig. 2.

#### 3.3. Investigation of the PPG emulsion in PFD

It was found that after the cessation of ultrasonic dispersion, most of the PPG is separated from PFD within 30 min. After the specified time, the PFD contains about 0.1 wt. % of dispersed PPG and the characteristic separation time of this dispersion is tens and hundreds of hours, it was proposed to call this system a quasi-stable dispersion.

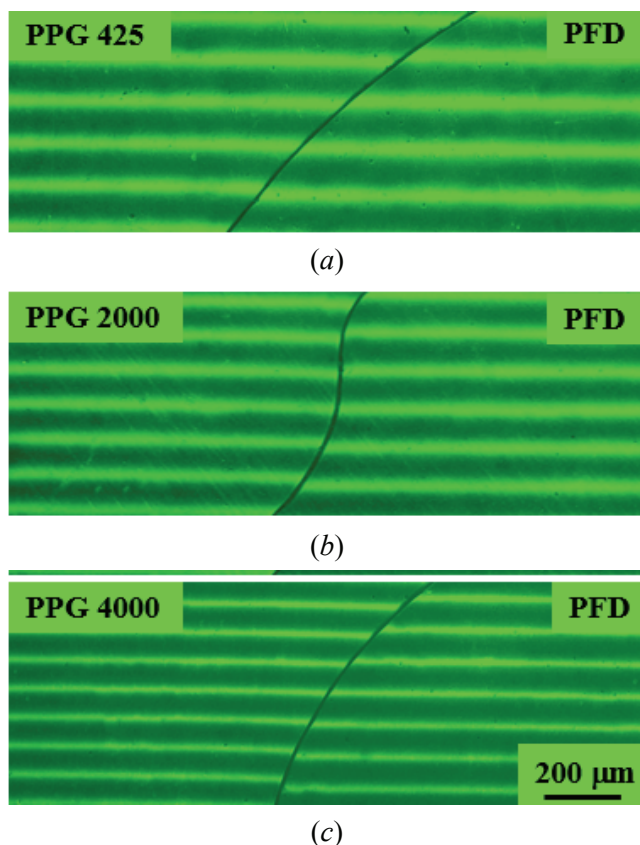


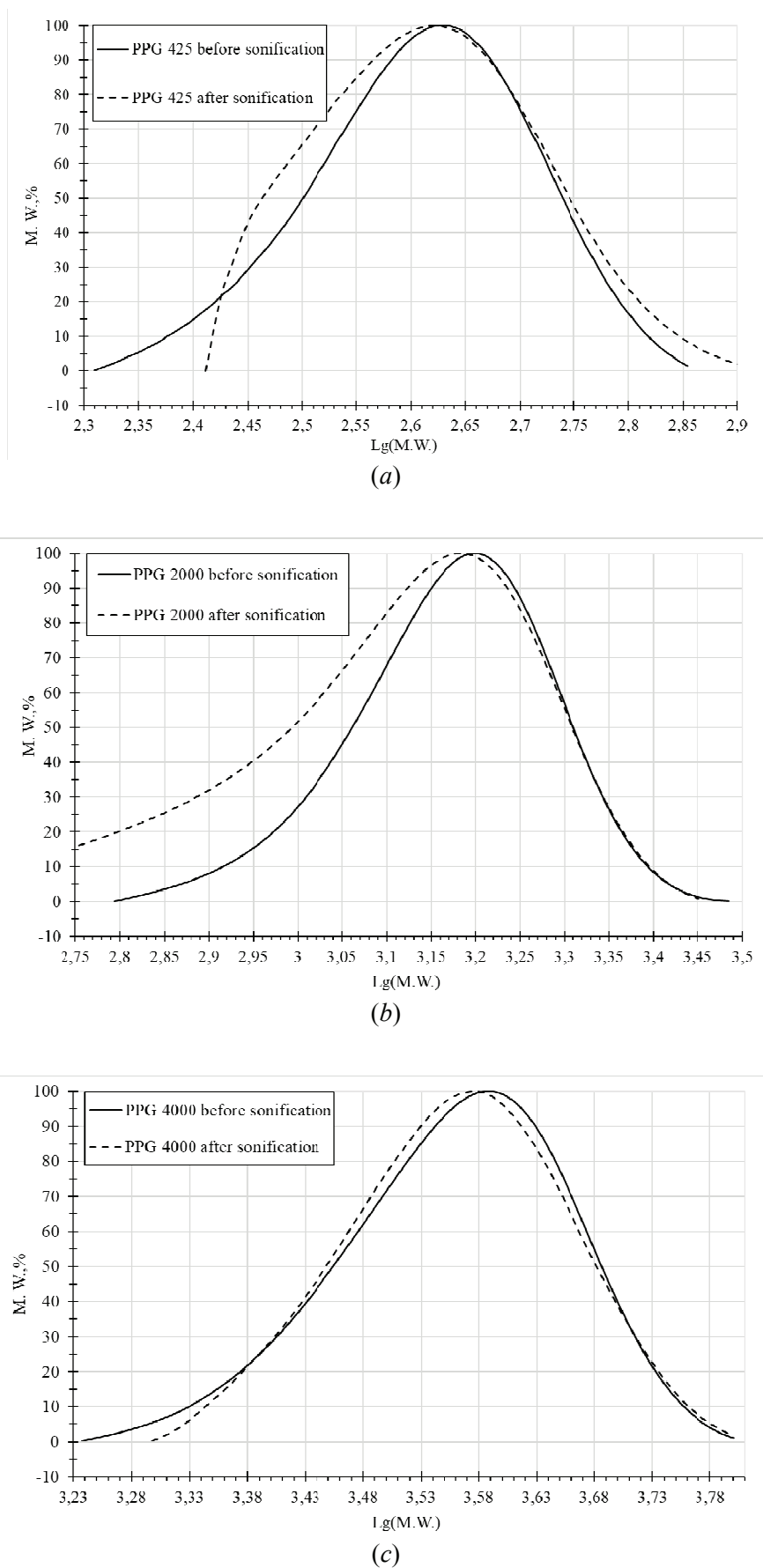
Fig. 1. Interferograms of systems PPG – PFD at (a) 45 °C, (b) 95 °C and (c) 62 °C

Table 3 shows the concentrations of PPG with different molecular weights in a quasi-stable dispersion, immediately after dispersion, 3 hours and a day after the cessation of ultrasonic exposure according to gravimetry.

Based on the studies to measure the concentration of PPG in emulsions, it can be concluded that the concentration of PPG in emulsions depends on the molecular weight of PPG and the time after ultrasonic dispersion. With a decrease in the molecular weight of PPG from 4000 to 425 Da, the concentration increases from 0.12 to 0.19 wt. %.

Table 2.  $M_w$ ,  $M_n$  and PDI before and after sonification

Substance	Before sonification			After sonification		
	$M_w$ , Da	$M_n$ , Da	PDI	$M_w$ , Da	$M_n$ , Da	PDI
PPG425	355	372	0.95	410	430	0.95
PPG2000	1374	1461	0.94	1417	1511	0.94
PPG4000	3388	3554	0.95	3461	3652	0.95



**Fig. 2.** The gel-penetrating chromatography of the PPG



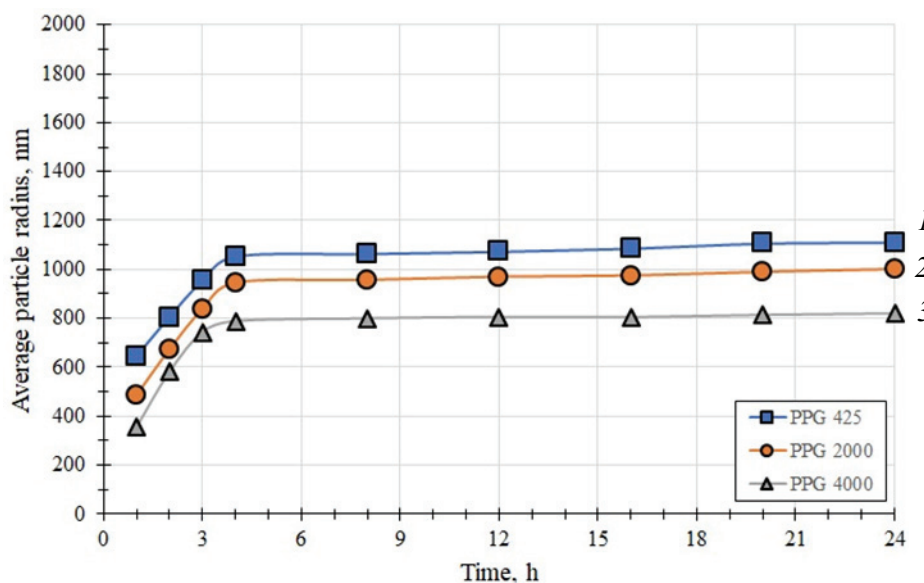


Fig. 3. Dependence of average particles radius in emulsions on time PPG 425 (1), 2000 (2), 4000 (3)

Table 3. Concentrations of PPG in emulsions of PPG – PFD over time

WT	Concentrations of PPG in PPG – PFD emulsions, wt. %		
	PPG 425	PPG 2000	PPG 4000
0.5	0.19	0.14	0.12
3	0.06	0.04	0.03
24	0.015	0.013	0.012

It was found that the concentration of PPG in a quasi-stable dispersion decreases over time by a factor of 3–4 in 3 hours after dispersion, the rate of change in concentration does not depend on the molecular weight of PPG.

Figure 3 shows the dependence of the average particle radius of dispersed PPG in PFD on the emulsion holding time. One hour after the end of the ultrasonic exposure, the characteristic particle radius is 350–650 nm, and after 24 hours – 800–1100 nm.

It is known that the characteristic depth of surface fluorination of polymers is about 0.1–10  $\mu\text{m}$  [6]. Since the liquid-phase fluorination of PPG in the system under study will occur at the interface, it is required to maintain the maximum area of the interface.

To carry out fluorination, it is advisable to use periodic ultrasonic dispersion of PPG in PFD at intervals of no more than 30 minutes to maintain the optimal concentration and surface area of the phase separation.

#### 4. Conclusion

Using laser microinterferometry, it was shown that PPGs of various molecular weights are insoluble in PFD, which was the reason for the need for dispersion using ultrasound. The absence of a statistically significant effect of ultrasonic dispersion on the change in the MWD of PPG was established.

The dependences of changes in concentrations and size of PPG particles on time were studied:

- the concentration of PPG in the emulsion decreases over time, and the particle size increases;
- the higher the PPG molecular weight, the lower the PPG concentration in quasi-stable emulsions, but the larger the average particle radius.

Since ultrasonic dispersion does not change the molecular weight of PPG, this process is applicable to provide a high specific interfacial area in the PPG – PFD system. The implementation of liquid-phase fluorination of PPG is advisable to carry out with continuous or periodic dispersion.

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#### 6. Conflict of interests

The authors declare no conflicts of interest.

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