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Two Dimensional Correlation Vibrational Spectroscopy and QM modeling applied to the study of Fluorinated PolymersStefano Radice¹, Alberto Milani², Chiara Castiglioni²¹ Solvay Solexis R&D Center, Viale Lombardia 20 20021 Bollate (MI) Italy,² Politecnico di Milano, Piazza Leonardo da Vinci, Milano, 20100, Italy

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Introduction

Fluorinated polymers play an important and innovative role in various technological and scientific industrial sectors. They may show outstanding and peculiar properties when high demanding requirements, such as thermal and chemical stability, are needed.

The development of new materials needs the support of analytical tools suitable to give precise and useful structural information.

In this respect vibrational spectroscopy (IR, Raman) contributed in the past and is still contributing in the determination of chemical composition, microstructure (sequence of monomers/chemical groups) and functional end groups [1-3]. More recently, the approach of Two Dimensional Correlation spectroscopy [4,5] has been successfully applied to the study of different phenomena:

- i) kinetics of chemical reactions (deblocking and crosslinking) [6]
- ii) spectral trends as a function of composition [7]
- iii) hydrogen bonded systems and aggregation phenomena [8]

The description of the above topics is here presented and summarised.

Materials and Methods

The examples reported are related to Perfluoropolyether products available on the market with the trademark names of FOMBLIN[®] and GALDEN[®]. Their chain backbone has the general chemical formula: $(CF_2CF_2O)_n(CF_2O)_m$ (statistical copolymers with $n>m$).

Most of their applications are in the field of high vacuum and lubrication technology.

Results and Discussion

The kinetic experiment (carried out on a sample inside the spectrometer) was aimed to follow the formation of the three dimensional urethane network. Fluorinated macromeric diols and hydrogenated isocyanate structures reacted to build up the material.

The kinetic model has been developed using intensity data and 2D correlation maps, mainly the asynchronous maps. The experiments and data analysis allowed to achieve information on reaction order and helped to select the best blocking agent and time/temperature conditions for effective crosslinking.

The normal modes analysis as a function of composition allowed to identify characteristic normal modes (Raman active) arising due to the presence of peroxide groups. The

overall effect of such moieties have been studied and analysed in details also by means of DFT modeling [7]. Indeed, QM modeling has been necessary to provide detailed eigenvectors description: as a matter of fact, most of the vibrations in fluorinated polymers may be considered as cooperative (not topologically localised) normal modes of vibration. The information obtained allowed to identify a localised normal mode due to the -O-O- bond stretching of peroxide moieties which is useful for analytical purposes.

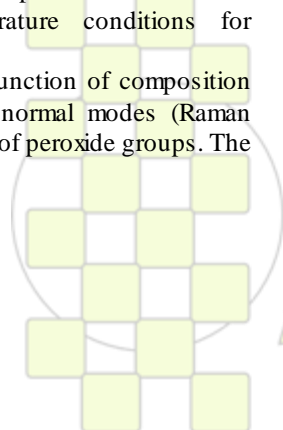
The third example is focused on the study of fluorinated macromers with amidic functional groups; we observed clear spectroscopic evidences of aggregation through hydrogen bonding. The nature and the amount of aggregates strongly depend on chemical environment, concentration and temperature. By means of accurate experimental data and QM modeling the experimental findings have been explained; three possible types of dimers and two types of trimers have been proposed for the description of the relevant aggregates. The 2D correlation approach has been applied using as perturbation both concentration and temperature [8]. The study allowed us to describe the fluorinated system also from a quantitative point of view, providing the aggregates distribution.

Conclusions

The approach combining IR and Raman experimental data with QM molecular modeling (DFT calculations) allowed to identify and assign normal modes suitable for analytical purposes in the characterisation of Fluorinated Polymers. The use of Two Dimensional Correlation spectroscopy provided us complementary piece of information with respect to usual 1D spectroscopic data and suggested further investigation on the observed spectral features.

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Solid State Properties of Fluorinated Polyimides Containing Perylene and Oxadiazole Moieties*Mariana-Dana Damaceanu, Radu-Dan Rusu, Maria Bruma*

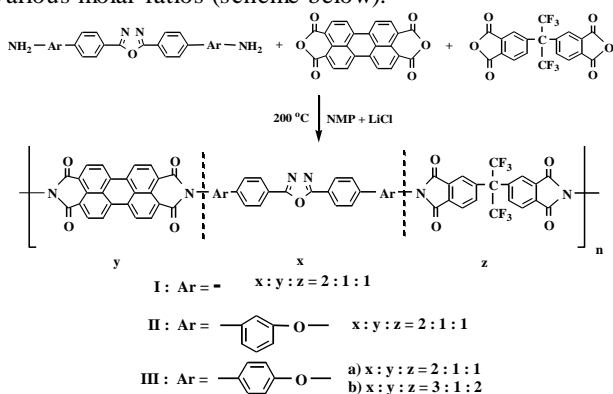
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e-mail: damaceanu@icmpp.ro**Introduction**

The increasing demand of advanced technologies for new materials offering high thermal, chemical and mechanical resistance and other special properties as electron-transporting ability, electroluminescence, optical and electrical conductivity stimulates the growing interest in aromatic polymers containing heterocyclic units [1,2]. The inclusion of imide rings together with other electron-rich rings, such as perylene, and with electron-withdrawing units, such as 1,3,4-oxadiazole, could be a good way to obtain polymers having a desired balance of properties [3]. However, the practical application of polyperyleneimides is very difficult due to their insolubility and lack of processability. In order to improve the solubility of perylene-containing polyimides, novel copolymers have been designed and synthesized by introducing flexible hexafluoroisopropylidene groups in the main chain. These polyimides based on aromatic diamines containing oxadiazole rings and a mixture of perylenetetracarboxylic dianhydride and hexafluoroisopropylidene-diphthalic dianhydride, dissolved in polar amidic solvents and gave flexible films, by casting their solutions onto glass plates. Here we present a study of these films by dynamo mechanical analysis (DMA), dielectric and X-ray photoelectron spectroscopy (XPS).

Materials and methods

Copolyimides **I**, **II** and **III** were prepared by one-step polycondensation reaction of three different aromatic diamines containing oxadiazole ring with a mixture of perylenetetracarboxylic dianhydride and 4,4'-hexafluoroisopropylidene-diphthalic dianhydride taken in various molar ratios (scheme below).

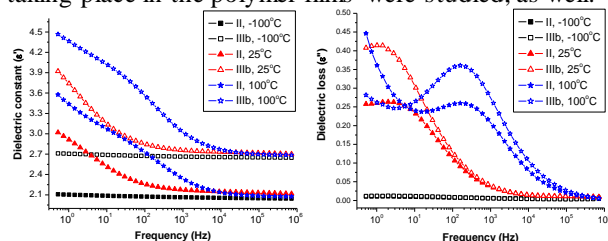


The reactions were carried out in NMP with 3.5% LiCl, at a concentration of 7% total solids, under nitrogen stream, at high temperatures (200-210°C). For comparison, a related copolyimide, **IV**, based on 4,4'-oxydianiline and a mixture 1:1 of the same dianhydrides was synthesized. All these polymers possess film forming ability. The free-standing films having a thickness in the range of tens of micrometers were flexible, tough, and maintained their integrity after repeated bending, except for films prepared from polymer **IIIa**, which were brittle. The properties of

these copolyimides such as solubility, thermal stability, glass transition, composition of the films, dielectric behaviour and subglass relaxations were investigated.

Results and discussion

The synthesized copoly(peryleneimide)s are soluble in a convenient aprotic amidic solvent which is NMP, at a concentration of 0.5-1%. The polymers are highly thermostable, with initial decomposition temperature being in the range of 465-475°C. The glass transition temperatures as evaluated by DMA using thin films, are above 300°C. The chemistry of the films was analyzed by XPS. The survey spectra for fluoropolymers **I-III** are dominated by C, O, N and F, with some minor components (Si, Cl, Li). Complex chemistry was observed in each film, and variations between the film samples were clear. It is likely that solvent, silicone and hydrocarbon contaminants are present, and perhaps water. Electrical insulating properties of the polymer films were evaluated on the basis of the dielectric constant, ϵ' and dielectric loss, ϵ'' and their variation with frequency and temperature. Figures below present the dependence of the real (a) and imaginary (b) part of the complex permittivity, on frequency, at low, moderate and high temperatures. The sub-glass relaxations taking place in the polymer films were studied, as well.

**Conclusions**

Thermostable polyimides containing oxadiazole and perylene units were prepared and thin films having a complex chemistry were made therefrom. The dielectric constant varies with frequency and temperature, taking low values even at high temperatures. The films displayed γ and δ relaxation processes connected with local movements of polymer chains.

Acknowledgements

The financial support provided by CNCIS-UEFISCDI through the Project PN II-RU, code TE_221, no. 31/2010 is acknowledged with great pleasure.

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Fluorene Based Core-Polymers for Efficient White OLED: Correlation between Molecular Structure and Photophysical Properties.

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Efficient white electroluminescence can be obtained from a fully miscible blend of core-type polyfluorene-based copolymers prepared by using Suzuki coupling reaction between a properly functionalized fluorene prepolymer coming on its turn from a Suzuki polycondensation and the di-bromide derivative of either a green or a red dye.[1]

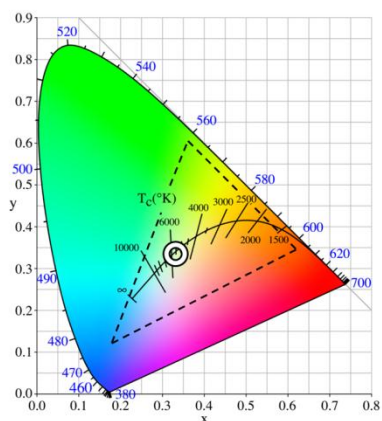


Fig.1 CIE 1931 chromaticity space, also showing Planckian locus

The chemical composition of the materials is a key factor to tune the emission colour, particularly the white shade (correlated colour temperature see Figure 1) which dramatically depends on the percentage of the three polymers constituting the blend. A deep molecular characterization of three polyfluorenes (PF) has been carried out combining different techniques such as (¹H- and ¹³C)-NMR, and MALDI-TOF MS. Their exact molar mass distributions were calculated applying the absolute calibration curves builds by SEC-MALDI TOF MS analysis of selected SEC fractions of opportune choice PF samples. More than ten clusters of homologous peaks separated by about 1039.2÷1039.6 Da which correspond the mass of the PF repeating units (1039.4 Da), were envisaged in the prepolymer samples, each cluster has been assigned to linear PF chains bearing different end groups corroborating NMR observations. Reactive boronate linear chains are present together with unprofitable bromide

terminated ones and un-reactive chains ending with phenyl or hydroxylic or hydrogen groups. Even more families are

present in the final core PF. The identification of macromolecules terminated with hydrogen, hydroxyl and phenyl groups suggests that, in accordance to the literature², side reaction occur during the Suzuki polycondensation reaction between dibromide and diboronate monomers. The formations of PF chains terminated with bis(boronic pinacol) diester in the prepolymer samples suggests that this group, in the Suzuki polycondensation, is more stable with respect to the bis(boronic 1,3-propanediol) diester end groups.

Moreover, by applying a gel permeation chromatography to separate the samples as a function of the chains molecular weight we were able to discriminate among the different situations obtaining in the high molecular weight range only the polymeric chains which contain in a core or end position the dye (red or green emitting depending on the chosen sample).

Photophysical characterization (absorption and photoluminescence) has been carried out on diluted solution of the different fractions to investigate intramolecular energy transfer mechanism as a function of both the molecular weight and the acceptor dye position within the polymer chain (core or end-type copolymers), and its effect on the overall photoluminescence quantum efficiency.

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Preparation of Fluoroalkyl End-Capped Oligomers Possessing Nonflammable and Flammable Characteristics in Silica Gel Matrices

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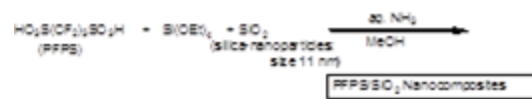
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From the developmental viewpoints of a higher thermally stable fluorinated polymeric materials, it is in particular interest to study the hybridization of fluorinated polymers with inorganic materials such as silica gels. For example, Lee et al. reported that PTFE [poly(tetrafluoroethylene)]/SiO₂ organic-inorganic hybrids can be prepared through a sol-gel process with tetraethoxysilane.¹ Kim et al. have very recently reported the preparation of perfluoroalkyl methacrylate polymer/silica organic/inorganic hybrids in supercritical carbon dioxide.² However, these fluorinated polymers/silica hybrids exhibit a clear weight loss behavior corresponding to the contents of parent fluorinated polymers in the hybrids around 600 ~ 700 °C or 400 ~ 600 °C, respectively.^{1,2} In a variety of fluorinated polymers, especially, fluoroalkyl end-capped oligomers are attractive materials, because they exhibit various unique properties such as high solubility, surface active properties, and nanometer size-controlled molecular aggregates which cannot be achieved by the corresponding non-fluorinated and randomly fluoroalkylated ones.³

Here, we have succeeded in applying these fluoroalkyl end-capped oligomers to nonflammable fluorinated polymeric materials through the sol-gel reactions with silica nanoparticles under alkaline conditions. Especially, in these fluorinated oligomers, fluoroalkyl end-capped N-(1,1-dimethyl-3-oxobutyl)acrylamide oligomer [R_F-(DOBAA)_n-R_F]/silica nanocomposites have been verified to exhibit a nonflammable characteristic even after calcination at 800 °C through the formation of hexafluorosilicate anion during the nanocomposite

reactions; although the parent fluoroalkyl end-capped oligomer can decompose completely around 500 °C. In contrast, no formation of hexafluorosilicate anion during the composite reaction affords a usually flammable behavior for fluoroalkyl end-capped acrylic acid oligomer [R_F-

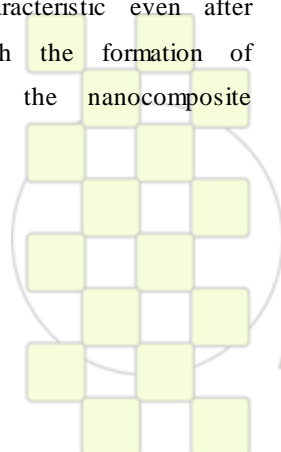


(ACA)_n-R_F]/silica nanocomposites.

In addition, we have found that not only R_F-(DOBAA)_n-R_F oligomer but also perfluoro-1,3-propanedisulfonic acid (PFPS) are applicable to nonflammable fluorinated materials through the sol-gel reactions with silica nanoparticles under alkaline conditions as shown in the following Scheme.

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Ionic Liquids : Structuration agents in a fluorinated matrix

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Introduction

The ability to create regularly shaped nanoscale objects which serve as the building block is an extremely important goal in materials science. One of the key issues is to design and create new polymer materials with unprecedented improvements in their physical properties. Different self-assembly pathways are described to lead to hierarchical structures formed from heterogeneous chemical species, like organic molecules, polymers, organic-inorganic nanobuilding blocks¹. Ionic liquids (ILs), which are organic salts with a melting point below 100 °C, with unique properties such as their chemical stability, excellent thermal stability, inflammability, low vapor pressure and high ionic conductivity have become more attractive in material science. This work reports for the first time the achievement of a nanoscale structuration from ILs into a polymer matrix. This structuration can be tuned by a wide choice of cation-anion combinations including pyridinium, imidazolium, and phosphonium as cation associated to iodide, bromide, or fluorinated anions. The preparation of IL nanostructured films from a fluorinated polymer solution could open many applications in energy and materials fields.

Materials and Methods

A general and simple method for the synthesis of a serie of organic halide and fluorinated salts is reported based on i) Iodide (I⁻), bromide (Br⁻) and hexafluorophosphate (PF₆⁻) combined phosphonium cations with one long alkyl chain denoted C₁₈P I, C₁₈P Br, C₁₈P PF₆⁻, respectively. ii) Iodide associated imidazolium cation with two long alkyl chains denoted C₁₈C₁₈Im I. iii) Iodide combined pyridinium salt denoted C₁₈Py I². The chemical structure of ILs combined to iodide anion is described in Figure 1.

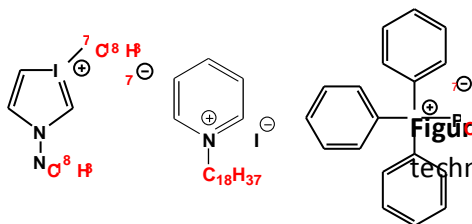


Figure 1. Chemical structure of synthesized ionic liquids To prepare supramolecular ionic networks, the three functional ionic liquids have been introduced in very low quantities (1 wt%) in a aqueous suspension of polytetrafluoroethylene (PTFE) under stirring. Then the suspension was spread on stainless steel plates to get 50 μm-thick wet layer. A thermal treatment at 400 °C for 10 minutes was applied to obtain the final polymer film.

Results and Discussion

The hydrophobic nature of polytetrafluoroethylene and the strong interactions between the ionic domains and the PTFE matrix generate a phase-separated morphology. It is

the balance of interactions between polymer medium and anion-cation pairs that leads to different morphologies³. TEM micrographs reveal different types of structuration which are tuned by the chemical nature of cation and of anion as well. For example, by using the same phosphonium cation combined with different anions, Figure 2 shows final morphologies varying between an aggregated one with the fluorinated or bromide anion and a fine structuration at nanoscale with the iodide conteranion. The morphologies characterized by SAXS and XPS analysis are comparable to those observed in ionomers⁴.

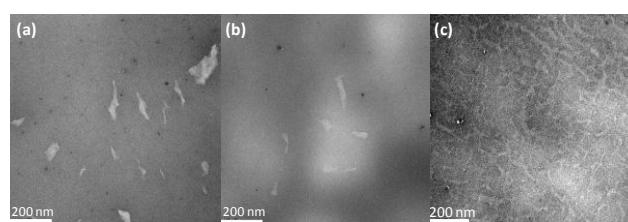


Figure 2. TEM micrographs of the nanocomposites (a) PTFE/C₁₈P PF₆⁻, (b) PTFE/C₁₈P Br⁻, (c) PTFE/C₁₈P I⁻

The distribution of ionic liquids in the polymer matrix plays a key role on the elongation at break of films. We have highlighted that the ‘spider web’ structuration leads to a dramatic increase of 190% of the elongation at break as shown in Figure 3. Thus, the formation of this network can play a retardant role against the beginning of catastrophic cracking.

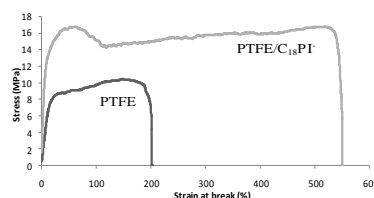


Figure 3 Effect of the phosphonium ionic liquid (1wt%) on the mechanical properties determined by uniaxial tensile tests at room temperature and 0.004 s⁻¹

Conclusions

The use of ionic liquids as functional building blocks based on pyridinium, imidazolium and phosphonium cations to achieve materials combining a structuration at nanoscale with the dramatic mechanical properties of the resulting ionomers has been successfully demonstrated for the first time in a fluorinated matrix.

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Study of Structural Features of Fluorinated Paraffins

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Fluoroparaffins are attractive as materials capable of enhancing tribological properties of objects they are applied to. Fluoroparaffins are superior to hydrocarbon lubricants in some aspects: they are generally more hydrophobic, more liophobic, and have smaller friction coefficient. The method used in this study for preparation of fluoroparaffins is based on fluorination of gaseous paraffin hydrocarbons of a specific molecular weight (ranging from C₁₂ to C₃₆). A sequence of technological processes was used for extraction of perfluorinated paraffins which were later studied using a number of physical methods in order to reveal their morphological, topological, and molecular structure. The parameters of the fluorination process were identical for samples with different molecular weights of the initial paraffin hydrocarbons.

All the samples prepared are wax-like materials with no marked morphological structure, but SEM micrographs reveal the presence of layered formations in them. XRD studies of the pristine paraffins and perfluorinated samples confirm the presence of those structures, which is indicated by reflections at small angles. According to the experimental data, the perfluorinated paraffins also contain topologically unordered formations, which is indicated by two halos in XRD patterns at $2\theta = 30-50^\circ$ and 72° . Such halos are specific for low molecular weight fractions of polytetrafluoroethylene. Peaks attributable to crystalline components (the most prominent of them is at $2\theta = 18^\circ$) which are specific for high molecular weight fractions of polytetrafluoroethylene are observed in patterns of high molecular weight paraffins.

A prominent dependence of thermal properties (weight loss onset temperature and melting temperature) of the perfluoroparaffins as function of their molecular weight was observed. Thermogravimetric curves of low molecular weight paraffins revealed smaller dispersion of molecular weights in them.

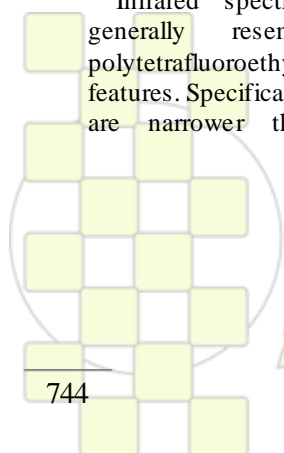
Infrared spectra of the fluoroparaffins studied generally resemble the IR spectrum of polytetrafluoroethylene but have some distinctive features. Specifically, the main bands (1228, 1154 cm⁻¹) are narrower than those in the spectrum of

polytetrafluoroethylene, which unmasks some other bands. The fluoroparaffins' spectra do not contain bands attributable to amorphous formations. Besides the bands attributable to CF₂ groups of the molecular helix, the spectra also contain components at 1371 and 986 cm⁻¹ which correspond to the terminal and lateral trifluoromethyl groups (CF₃), respectively, as follows from quantum chemical calculations for fluorocarbon conformer models. There are also bands which can be ascribed to hydrocarbon groups.

The samples were studied using high resolution magic angle solid state nuclear magnetic resonance (MAS NMR) on ¹H, ¹³C, and ¹⁹F nuclei. Attribution of peaks in the experimentally acquired NMR spectra was performed via comparison of the experimental data with the values of chemical shifts calculated using quantum chemistry. The studies revealed that the fluorination process does not result in complete substitution of hydrogen atoms by fluorine, and the spectra of all the samples contained peaks attributed to protons. The observed resonance lines indicate the presence of CH₂-, CFH-, CH₂F-, and CHF₂ groups. The ratios of functional groups in the samples prepared from paraffin hydrocarbons of different molecular weights were determined based on the intensities of the respective NMR peaks. These data are confirmed by ¹³C spectra. ¹⁹F NMR spectra reveal the presence of CF₃ groups in the samples; concentration of these groups depends on molecular weight of oligomers which comprise the fluoroparaffins.

The solubility of fluoroparaffins in supercritical carbon dioxide has been measured at temperatures of 318 - 383 K in the pressure range of 10 - 80 MPa and it was not lower than 50 g/L.

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Fluoropolymer dispersions: new environment-friendly products and technology*S. Musio**, V. Kapeliouchko, T. Poggio

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Polytetrafluoroethylene (PTFE) has seen increasing demand in sophisticated industrial applications since 1938, due to its thermal and chemical inertness, release properties, and outstanding dielectric characteristics¹. Aqueous dispersions of PTFE are particularly suitable for cookware antistick coatings and endless conveyor belts for the food industry: such dispersions are commonly obtained via emulsion polymerization in the presence of a non-telogenic perfluorinated anionic emulsifier, leading to 150-300 nm particles. Alternatively, a proprietary Solvay Solexis technology^{2,3,4} using microemulsion polymerization allows the synthesis of 10-60nm particles, which are advantageously exploited in bimodal dispersions. This results in a more compact and less porous PTFE film structure leading to better application performances in terms of coating appearance, mechanical strength, and durability.

Recent developments in PTFE dispersions combine knowledge on new fluorosurfactants developments with yet available processes to reduce the content of fluorosurfactant in the dispersions⁵ and with appropriately selected phenol-free non-ionic surfactant to eventually obtain environmentally friendlier PTFE dispersions that match or even improve the processing performance compared to standard products.

The formulation of fluoropolymer dispersions, purified from anionic fluorinated surfactants used in polymerization, requires re-design of specific ingredients in order to maintain the performance profile of the product in the whole range of applications, e.g. coating, impregnation, etc.

Starting from the colloidal properties of the initial systems, this presentation discusses in particular stability to

shear and sedimentation as well as rheological behavior of PTFE dispersions.

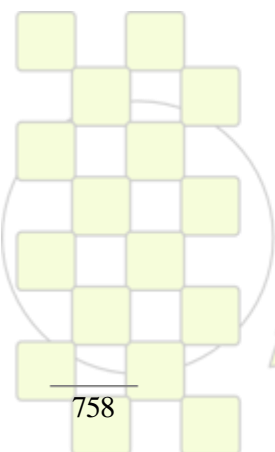
In particular the environmentally friendly fluoropolymer dispersions obtained by substituting APE surfactants with “Green” Ethoxylated Alcohols and by extracting perfluorinated surfactants are discussed, which impart the following features:

- More newtonian rheological behavior resulting into better properties under a wider range of applicative conditions of temperature and shearing.
- Lower surface tension, both static and dynamic values, which imparts outstanding wetting ability especially under critical high-speed impregnation conditions.
- Excellent stability to shear and sedimentation due to better interaction of the surfactant with the polymer surface: the adsorption behavior is very similar to that of APE surfactants

Cleaner thermal degradation of the surfactant system resulting in higher quality of the final objects.

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Peculiarities of water emulsion copolymerization of tetrafluoroethylene with perfluoro(3,6-dioxa-4-methyl-7-octene)sulfonyl fluoride to obtain proton conducting copolymers

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The copolymerization of tetrafluoroethylene with functional perfluorinated comonomers in aqueous emulsions was attempted in a series of recent studies [1-3].

In this report we present the analysis of kinetic features and mechanistic study of the copolymerization of these monomers in water emulsion systems.

An important condition providing a water emulsion copolymerization of the considered monomers is their preliminary dispersing according to various procedures. A conventional pre-emulsification method is found to provide copolymers with the composition remaining almost constant up to high (~85%) conversions of a functional comonomer featuring with a low reactivity.

We studied the changes in the dispersity of the initial monomer droplets and resulting polymer particles in the latex at different monomer conversions by light scattering using a Malvern Zetasizer Nano-ZS analyzer.

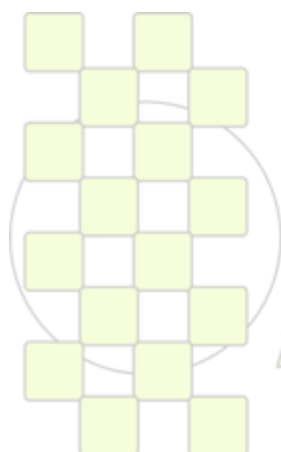
The dispersing of monomer droplets and polymer-monomer latex particles are found to proceed during the copolymerization.

A mechanism of elementary reactions at copolymerization is suggested upon the analysis of the solubility of the polymerization system components and the resulting copolymer in the water emulsion system.

The obtained data indicate a promising potential of water emulsion copolymerization of these monomers for obtaining a high quality copolymer useful for the production of proton conducting membranes.

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Nanocomposite Membranes Based on Nafion and TiSiO₄ nanoparticle

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Fuel cells are one of the most promising alternative power sources, with efficiencies of up to 60%, higher energy densities relative to batteries, and the ability to operate on clean fuels while producing no pollutants. Among fuel cells, Proton Exchange Membrane (PEM) Fuel Cells have received particular attention as a possible mobile electrical power source with high energy density. Proton exchange membrane is the key component of the PEM fuel cell for transferring protons from the anode to cathode as well as providing a barrier to the fuel gas cross-leaks between the electrodes.

Nafion is the PEM material most frequently used for this type of application because of its high proton conductivity, excellent mechanical properties, good chemical stability and commercial availability. However, the high cost, low stability at high temperatures, low conductivity at low humidity or high temperature limits the extent of its further application. Several approaches have been used to overcome this problem, such as the use of nanometer size inorganic filler in the Nafion matrix. The results showed that the modification of the polymer host membrane by the incorporation of hygroscopic oxides, such as ZrO₂, SiO₂, and TiO₂ particles, into Nafion has effectively extended the working temperature range. The inclusion of inorganic fillers improves the mechanical properties, the membrane water management and also contributes to inhibiting the direct permeation of reaction gases by increasing the transport pathway tortuosity.

Among the inorganic materials used in this field, TiO₂ and SiO₂ nanoparticles is good candidate as hydrophilic filler for the polymer membranes because it helps to maintain a suitable hydration of the membrane under fuel cell operating conditions, and the mechanical properties are improved.

In the present study, Nafion/Titanium Silicon Oxide (TiSiO₄) nanocomposite membranes for use in PEM fuel cells were investigated. Composite membranes were prepared using the recasting procedure and membrane thickness around 80 μm was obtained from 10 wt.% TiSiO₄ loading. Nafion/TiSiO₄ nanocomposite membranes characterized by FTIR, thermal analysis, water uptake, XRD, SEM, EDS analysis and single cell performance. The introduction nanometer size TiSiO₄ supplies the composite membrane with a good thermal resistance and electrochemical performance. The physico-chemical properties studied by means of scanning electron microscopy (SEM) and X-ray diffraction (XRD) techniques have proved the uniform and homogeneous distribution of TiSiO₄ and the consequent enhancement of crystalline character of these membranes.

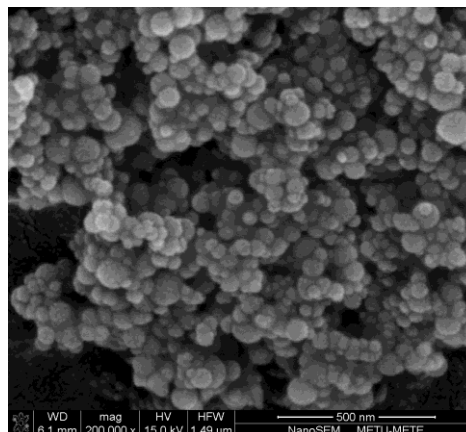
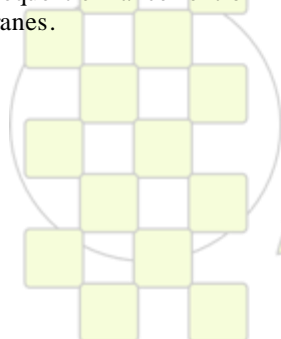


Figure 1. SEM image of TiSiO₄

The energy dispersive spectra (EDS) analysis indicated that the distribution of TiSiO₄ on the surface of the composite membrane was uniform. The membranes were tested in a single cell with a 5 cm² active area operating at 70 to 120°C. The results show that Nafion/ TiSiO₄ are promising membrane material for possible use in proton exchange membrane fuel cells.

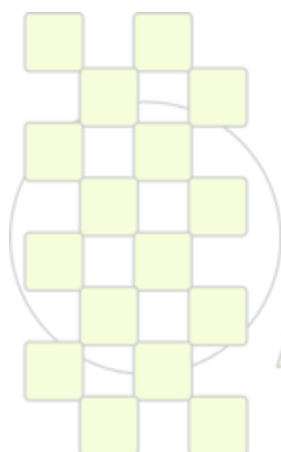


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On the Morphology of Drawn UHMWPE Gel Films and PTFE Extrudates*H. M. Shabana*Prof. of Experimental Physics, Applied Science Dept., College of Technological Studies,
PAAET, P. O. Box 42325, Shuwaikh 70654, KUWAIT.*e-mail: hmshabana@hotmail.com***Abstract**

Two high performance polymers, polytetrafluoroethylene (PTFE) and Ultra high molecular weight polyethylene (UHMWPE) are investigated using several tools. The failure behavior exhibited by both polymers at different extrusion rates are discussed as a function of the time factor. The time at which both polymers failed is shown to be constant. These results reflect that the failure is independent on the rate of stretch, at least in specific range of stretching rates. The change of the maximum attainable draw ratio with the initial polymer concentration is investigated at different temperatures. At 130 °C, the maximum attainable draw ratio increases as the initial polymer concentration decreases. The effect of drawing on the melting endotherm at different rates is also demonstrated for the drawn UHMWPE. Two peaks are observed, and may represent two components of morphology within the film and not a reorganization phenomenon. The second peak starts to disappear at draw ratio 4 and completely disappear at draw ratio 7. The melting point of the drawn gel films is shown to be nearly the same. The changes in morphology of the stretched UHMWPE are investigated by the scanning electron microscopy. The morphological changes in relation to specimens with different concentrations are given. Disentangled network and fibril structure are formed at the final stage. Several attempts are made to etch and to replicate UHMWPE to reveal the internal microstructure using the transmission electron microscope. Permanganic etching and both one and two-stage replication methods are used for this purpose.

Keywords: PTFE, UHMWPE, mechanical drawing, DSC, electron microscopy



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Nonvolatile Memory Transistors using Ferroelectric P(VDF-TrFE) and Printed Semiconducting Channel

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Organic non-volatile memories are the emerging research field due to its unique characteristics in charge storage properties and a relatively low manufacturing cost. Conjugated molecules and solution processable charge storage materials enable to realize the memory device by simple and cost-effective solution processes such as spin coating or various graphic art printing techniques. Among the many possible configurations for ONVMs, organic field effect transistors (OFETs)-based memory has many advantage including non-destructive read-out, complementary integrated circuit architectural compatibility, and single transistor realization.

To realize high performance ferroelectric OFET memory, ferroelectric polymer materials must show both robust mechanical properties as a gate dielectric and large dipole polarization as a memory element. Poly(vinylidene fluoride-trifluoroethylene) [P(VDF-TrFE)] copolymer is one of the promising materials to fulfill both properties at once.

There have been many reports on the memory characteristics of P(VDF-TrFE) with metal-ferroelectric-metal, metal-ferroelectric-insulator-semiconductor capacitors, or OFETs. Although these results clearly suggest a high feasibility of P(VDF-TrFE) for nonvolatile memory, there are a few challenges must be addressed such as a high programming voltage, low switching speed, and insufficient data retention time and various approaches including modifications of material and/or device structure have been proposed.

In this study, we demonstrate a low voltage operated top gated ferroelectric polymer transistor memory with a inkjet-printed organic semiconductor active channel and a poly(vinylidene fluoride-trifluoroethylene) ferroelectric gate insulator. Key features of our ferroelectric memory devices are all-solution process and a relatively low operating voltage. The low operating voltage was achieved by single P(VDF-TrFE) dielectric layer and the memory device typically operated a low gate and source-drain bias below 15 V.

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This project was supported by the IT R&D program of MKE (2008-F052-01, Development of Next Generation RFID Technology for Item Level Applications)

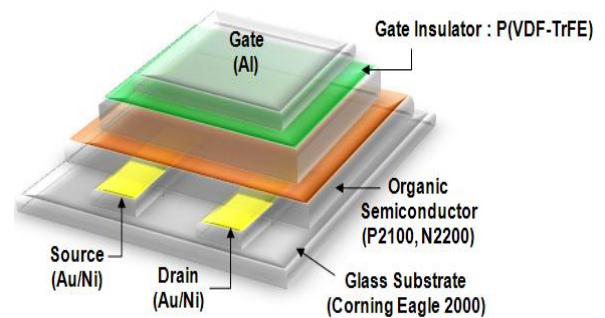


Figure 1. Schematic representation of the device configuration of a top-gate/bottom-contact polymer field-effect transistor.

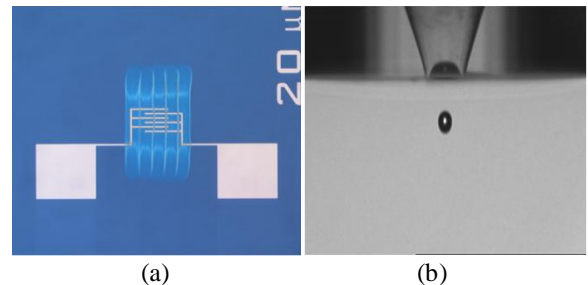


Figure 2. (a) Optical image of inkjet-printed nonvolatile memory TFTs. (b) High speed CCD camera images of inkjet droplet formation.

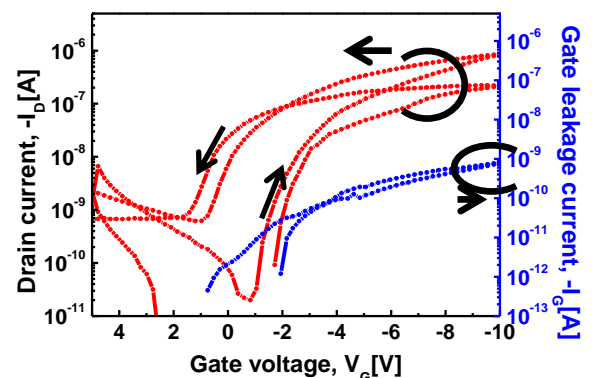


Figure 3. Transfer curves of top-gate and bottom-contact memory transistors with P(VDF-TrFE) film.

Design and Synthesis of Low Refractive Index, Organosoluble, and Thermally Stable Fluorinated Polyamides Having *Ortho*-Linked Aromatic Units in the Main Chain

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Introduction

Wholly aromatic polyamides (PAs) are considered to be high-performance materials due to their high thermal stability, chemical resistance and outstanding mechanical properties, which make them useful for advanced technologies. However, most PAs are usually difficult to process due to their limited solubility in common organic solvents and high glass-transition temperatures. Therefore, many efforts have been made to improve the processing characteristics of these relatively intractable polymers. It has been demonstrated that incorporation of both flexible ether linkages and bulky naphthalene units into the polymer backbones can enhance the solubility and processability of aromatic polyamides without any significant reduction in thermal stability [1]. Another attractive approach employed to increase the solubility of polyamides is the incorporation of less symmetric units such as *ortho*-catenated aromatic rings in the main chains which leads to a reduction in crystallinity [2]. Recently, considerable attention has been devoted to the synthesis of fluorinated aromatic polyamides, especially the trifluoromethyl (CF₃)-containing poly(ether amide)s (PEAs) [3]. It has been recognized that the incorporation of bulky –CF₃ groups into PA backbones resulted in an enhanced solubility and optical transparency together with a lowered refractive index and dielectric constant, which was attributed to the low polarizability of the C–F bond and the increase in the free volume [4]. As part of our recent efforts to develop high-performance fluorinated polymers with excellent solubility and high thermal stability, as well as low refractive index and low birefringence for advanced optical and electronic applications, the current work reports the synthesis and characterization of a series of fluorinated PEAs from a high-purity CF₃-containing diamine, (DA), with various commercially available aromatic dicarboxylic acids.

Materials and Methods

The new CF₃-containing bis(ether amine), 1,1'-sulfide-bis-[(2-trifluoromethyl)4-aminophenoxy] naphthyl ether, was prepared in a two-step process. The first step is the chloro-displacement reaction of 2-chloro-5-nitrobenzotrifluoride with the potassium phenolate of 1,1'-thiobis(2-naphthol) formed in situ by the treatment with potassium carbonate in DMSO. The target bis(ether amine) was readily obtained in high yields by the Pd/C-catalyzed reduction of the intermediate dinitro compound (DN) with hydrazine hydrate in refluxing ethanol. The direct polycondensation was adopted here to prepare aromatic poly(ether amide)s.

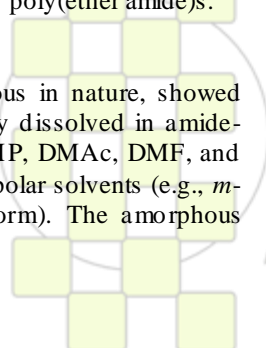
Results and Discussion

All of the polymers were amorphous in nature, showed good solubility and could be readily dissolved in amide-type polar aprotic solvents (e.g., NMP, DMAc, DMF, and DMSO) and even dissolved in less polar solvents (e.g., *m*-cresol, THF, pyridine, and chloroform). The amorphous

nature and good solubility of these PEAs can be attributed to the effect of the packing-disruptive –CF₃ and naphthyl groups and the *ortho*-linked structure, which could inhibit close packing and reduced the interchain interactions to enhance solubility. The presence of flexible ether and thioether linkages in the bis(ether amine) moiety also contributed to the enhancement in solubility. The thermal properties of the PEAs were evaluated by thermogravimetry analysis (TGA) and differential scanning calorimetry (DSC). The *T_g* values of aromatic PEAs were in the range of 221–263 °C, which follows the decreasing order of the chain flexibility and steric hindrance of the polymers backbones. The temperatures at 10% weight loss (*T*₁₀) values of the PEAs were in the range of 483–537 °C in nitrogen and in the range of 461–527 °C in air, respectively. The amount of residue of all PEAs at 700 °C in nitrogen atmosphere was higher than 50%. The data from thermal analysis showed that the resulting PEAs had fairly high thermal and thermooxidative stability. The in-plane (*n*_{TE}) and out-of-plane (*n*_{TM}) refractive indices of the PEA films measured at 1320 nm range from 1.5633 to 1.5844 and 1.5578 to 1.5754, respectively. In general, the low refractive indices of the resulting polymers are obviously attributed to the introduction of flexible ether and thioether linkages and large free volume of the C–F bond that interrupts chain packing and increase free volume. In this work, all the PEA films exhibited positive birefringence ($\Delta n = 0.0055\text{--}0.0097$), indicating that the molecular chains were preferentially aligned in the film plane. The low birefringence of the PEAs can be mainly attributed to the flexible linkages, which effectively reduce the in-plane orientation of the PA main chains. The dielectric constants (ϵ) of the polymers can be estimated from the refractive index according to Maxwell's equation ($\epsilon = n_{AV}^2$). All the synthesized PEAs had relatively low ϵ (2.44–2.50).

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Gas Separation Membranes Derived From Rigid, High-Free-Volume, Fluorinated Polyimides.

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Introduction

In the last decades, a huge research effort has been employed to prepare polymer membranes for gas separations that improve the well-established trade-off between permeability (gas flux) and selectivity (separation capacity), also known as Robeson's upper bound [1]. Aromatic fluorine-containing polyimides, mainly those having the group hexafluoroisopropylidene, are some of the most attractive and promising gas-separation materials. They do not only present a favorable balance of gas permeability and selectivity but also excellent thermal, chemical and mechanical properties.

Recent research in this subject [2, 3] has shown that the simultaneous increase in main chain rigidity (strongly hindered ring rotation) and fractional free volume, FFV, (low packing density) provides polyimides with high permeability and good selectivity.

This work shows the synthesis of a series of polyimides derived from the twisted, non-coplanar diamine 1,4-bis(4-amino-2-trifluoromethylphenoxy)2,5-di-*tert*-butyl benzene (CF₃TBAPB). The effect of trifluoromethyl (CF₃) groups on the transport properties has been studied by comparing with analogous polyimides without CF₃ moieties (TBAPB) [2].

Materials and Methods

A series of polyimides was synthesized from diamine CF₃TBAPB and three commercial dianhydrides following the classical one-step polyimidation methods. The structures are shown in Fig. 1. Polyimides were obtained by both thermal (H) and chemical (C) imidization of the polyamic acid precursor. The chemical structure of polyimides was confirmed by conventional techniques such as ¹H-NMR, ¹³C-NMR and FTIR.

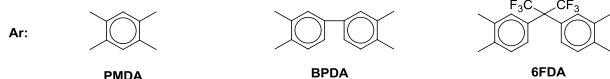
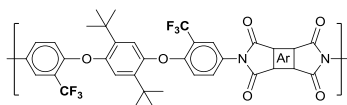


Fig.1. Chemical structure of polyimides

Polymer films were heated above their glass transition temperature, T_g, under a nitrogen atmosphere to strip off the residual solvent. Structural characterization of films was performed by WAXS. FFV was calculated from density data obtained by a buoyancy method [2].

Thermal stability and T_g, were determined by TGA and DSC, respectively.

Pure gas permeability coefficients (P) were determined by using a barometric permeation method at 30 °C and 3 bar pressure. Ideal selectivity for two pure gases was defined

as $\alpha(A/B) = P_A/P_B$. For permeation experiments, O₂, N₂, CH₄ and CO₂ were used.

Results and Discussion

All polyimides showed high thermal stability, with decomposition temperatures above 480 °C, and T_gs higher than 270 °C. The reaction of diamine CF₃TBAPB with rigid dianhydrides yielded polyimides with much higher FFV than the analogous TBAPB series.

The performance of these membranes for gas pair CO₂/CH₄ is shown in Fig. 2. In general, the new polyimides exhibited higher permeability to specific gases, with good selectivity, than those analogous without CF₃ groups.

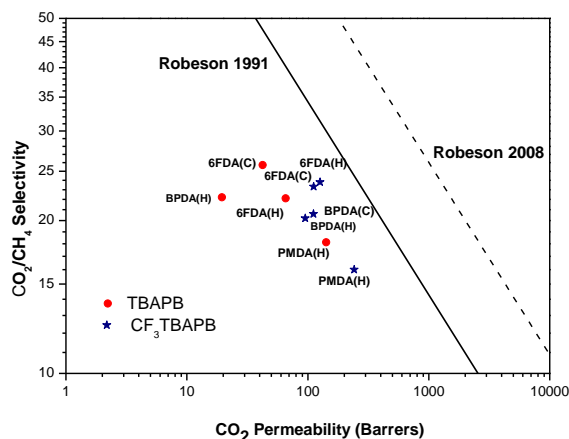


Fig.2 CO₂/CH₄ Selectivity versus CO₂ Permeability

No clear relationships between membrane properties and imidization method were found.

Conclusions

Novel polyimides having high FFV and high molecular chain rigidity have been obtained by a right combination of CF₃ and *tert*-butyl pendent groups on a diamine moiety. These fluorinated polyimides showed an excellent balance for gas separation, particularly for O₂/N₂ and CO₂/CH₄.

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Acknowledgements

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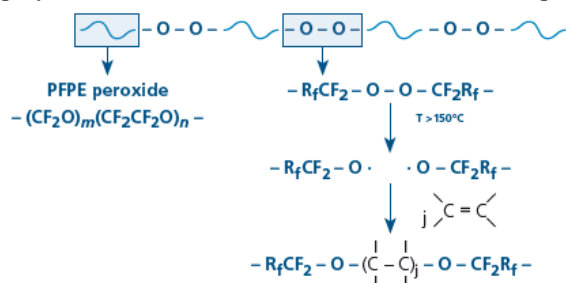
Innovative perfluoropolyether-based copolymers: another breakthrough in fluorine chemistry

M. Avataneo, P.A. Guarda and G. Marchionni

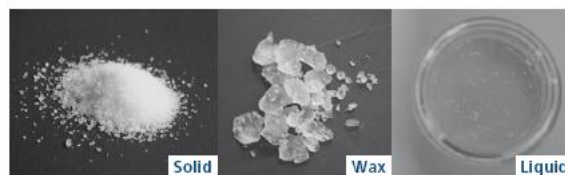
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Solvay Solexis has always been engaged in answering to the most challenging needs of high technology markets by developing new and innovative fluorinated products in the field of fluoropolymers [1], fluoroelastomers [2] and fluorinated fluids [3]. Very recently, a new technological platform has been introduced for the synthesis of a pioneering class of perfluoropolyether (PFPE) based copolymers [4, 5] that will fill many of the gaps existing today in markets not currently served by PFPEs. This new chemistry, based on the radical reaction of peroxidic perfluoropolyethers [6] with unsaturated fluorocompounds, can be exploited for the preparation of a huge variety of copolymers not achievable with conventional techniques:



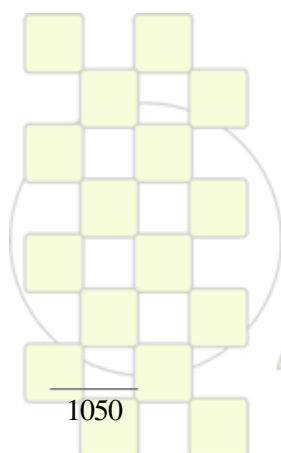
Due to the novelty of these materials, applications are endless, from thin film lubrication to gel based greases [4], to PFPE thermal stabilizer additives [5], polymer processing aids [7,8] and low Tg perfluoroelastomers [5], just to name a few. Many other applications are still under evaluation and development.



PFPE-TFE block copolymers: from solid to liquid

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Validation of an elasto-viscoplastic model for polyvinylidene fluoride (Pvdf)

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Introduction

Polyvinylidene fluoride (PVDF) copolymer is a thermoplastic of great potential to structural applications, such as internal pressure barriers of flexible risers used in offshore petroleum industry and also for lining of corroded onshore oil pipes [1,2]. The time-dependent properties of PVDF are still a subject of concern when higher temperatures are considered. Mechanical properties of polymers are strongly influenced by strain, temperature and time or frequency [3], thus it is important to study the viscoplastic behavior to assess the response of a polymeric structure in structural engineering applications. The aim of this study is to test a constitutive model to be employed in the numerical simulation of PVDF under time dependent thermo-mechanical loading.

Materials and Methods

In this case, the two layer visco-plastic model of Abaqus Software will be tested. For model implementation, several mechanical parameters must be obtained through tensile and relaxation tests in different conditions. The model parameters, such as elastic, viscous and plastic modulus were determined through tensile tests at 25, 40 and 60 °C and strain rates from $1.2 \cdot 10^{-5} \text{ s}^{-1}$ to $1.2 \cdot 10^{-1} \text{ s}^{-1}$.

Results and Discussion

Tensile results showed a decrease of elastic modulus and maximum stress with increasing temperature or decreasing strain rate. The relaxation tests were made at

25, 40 and 60 °C and initial strains from 3 to 20%. Through these results it was possible to establish a theoretical stress-strain curve for almost zero strain rate to be used in the constitutive model. Also, the time dependent stresses under different temperatures were proposed through the Norton-Hoff equation. The relaxation tests were correlated with the numerical results using a nonlinear finite element modeling under the proposed constitutive model.

Conclusions

The employed methodology generated good correlation within the beginning of the relaxation tests but showed an increasing discrepancy with time for the predicted stresses. These discrepancies were reduced with the manipulation of the convergence parameters and time increments.

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Ionic conductivity vs. thickness on the cast Nafion® polymer

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1. Introduction

Perfluorosulfonic acid membranes such as the Nafion are currently used as the electrolyte due to their favourable chemical and mechanical stabilities together with their high proton conductivity [1]. The conductivity of fully hydrated Nafion® membranes plays a key role in the performance of PEM fuel cells.

Many groups have previously studied the conductivity of Nafion® membranes and a large quantity of data has been published. The main difficulty in the analysis and comparison of these works is related with the utilization of different measuring methods. It is very difficult to rationalize all these data, but it appears clear that conductivity measurements are influenced by a number of parameters such as: (a) cell geometry, (b) technique employed, (c) electrolyte and (d) sample preparation method [2]. Moreover, the hydration of the material has also introduced differences that are well known in the conductivity measurements. So, the method to obtain the conductivity has to be taken into account.

On the other hand, there are several strategies to provide satisfactory proton conductivity and fuel cell performance. In the optimization to reduce the resistance of the membranes is usual to reduce the thickness.

The purpose of the present work was to study and to rationalize the experimentally observed increase of Nafion conductivity with membrane thickness that has also been obtained by other authors [2-4].

2. Materials and methods

Nafion polymer iso-propanol solutions were obtained from Ion-Power (USA). Adequate amounts of the solution were cast on Petri dish in order to obtain adequate thickness of the membranes. Solvent evaporation at 70°C during 24 h, and annealing of the membrane at 125 °C during 90 min were followed.

To measure the ionic conductivity of the membranes, they were conditioned by washing with water, H₂O₂ and diluted HCl, in hot conditions.

Ionic conductivity measurements were performed in a Zahner IES, in a frequency range of 1 Hz – 499 kHz, by sandwiching of the sample between two gold electrodes of 20mm of diameter at 2 bars of pressure and 90 °C.

3. Results and discussions

Ionic conductivity of one-hundred membranes was studied. Measurements were obtained following Eq. 1,

$$\sigma = L / (R * S)$$

Eq.1

where, σ (S/cm) is the conductivity, L (cm) is the thickness of the membrane, R (Ω) is the resistance, and S (cm²) the measured area.

Obtained results are in agreement with those recently published by Tsampas *et al.* [4]. They were found that the conductivity of Nafion contains two components, one due to proton migration in the aqueous phase, the other due to proton tunneling between adjacent sulfonate groups in narrow pores.

In the present study, several membranes with different thickness were synthesised and their ionic conductivity was measured. In Fig.1 is shown the correlation between ionic conductivity and thickness of cast membranes. Results were fit to a liner regression with a coefficient of adjustment of R = 0.94.

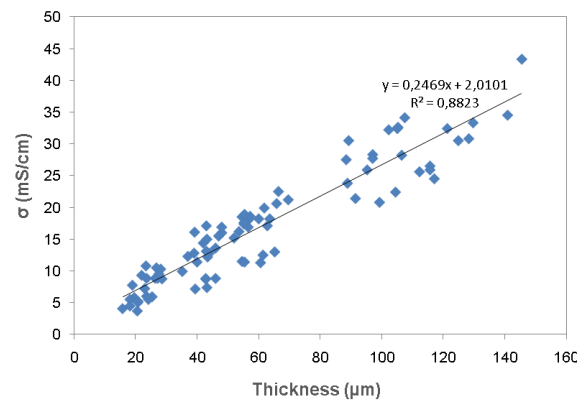


Fig.1. Variation of ionic conductivity with the thickness of the Nafion cast membrane.

4. Conclusions

The ionic conductivity value of Nafion cast membranes increases linearly with the membrane thickness in the range of 20 to 150 μm. This effect shows that a skin conductivity layer could be produced.

5. Acknowledgements

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Quantum-chemical study of the low molecular polyethylene fluorination

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Fluoropolymers occupy an important place among polymer materials and are assigned to functional materials due to their many applications. The low molecular specimens, that already have practical applications for coatings, nanofilms, composites and nanocomposites, have attracted considerable interest among varying fluoropolymers. One of ways to obtain the low molecular fluoropolymers is fluorination of hydrocarbon materials, such as paraffin and low molecular polyethylene. Quantum chemical calculations can be a good tool to study the processes of formation of these polymers. With a high degree of confidence you can get information on how to modify material, topological parameters of these systems, the preferred configurations and, finally, to a great extent help in the interpretation of experimental data obtained by the methods of vibration spectroscopy, NMR, and XPS which are commonly used to control the process of preparation of such polymers and study the molecular structure of the resulting materials. The results of quantum chemical calculations of the model system $C_{10}H_{22}$ with successive substitution of hydrogen by fluorine atoms are presented in this work. The energy of fluorination process, topological parameters, NMR¹⁹F, NMR¹³C, NMR¹H and vibration spectra of model systems of $C_{10}F_nH_{22-n}$ ($n = 1-22$) were calculated. The nature of the signals in the NMR¹⁹F, NMR¹³C spectra and band assignments in IR spectra of the calculated model molecules were made. *Ab initio* Hartree-Fock (HF, basis of 6-31G)

and density functional (DFT (B3LYP, basis of 6-

311+G(d)) methods was used for calculations. The calculation method was adopted by the carried out test (molecules with known parameters) calculations. The obtained results are very close to experimental data for compounds which these molecules simulated.

Conclusion

The obtained calculations showed.
- At the fluorination of the polymer chain the intrachain substitution of hydrogen to fluorine gives the most stable configuration and the both fluorine atoms belong to the common carbon.

- At a partial fluorination of the polymer the new bands corresponding to vibrations of the CF, CF₂, and CF₃ groups appear in the vibration spectra. The structure and position of the bands, that characterize the vibrations of hydrocarbon groups, change due to redistribution of electron density in the whole molecule at substitution of hydrogen to fluorine. Noticeable changes in the IR spectrum occur even in the region of stretching vibrations of C-H at 3000-2800 cm⁻¹ (Fig.1), therefore, one can easily discern whether the system has formed by a composite of the core-shell, or modified form of the polymer is created.

- NMR¹⁹F and NMR¹³C spectra differ at changing in number of substituted hydrogen atoms and the place of substitution in the polymer chain. Differences are rather obvious and in the NMR¹⁹F spectra and NMR¹³C spectra (Fig.2), therefore the NMR spectra can be an indicator of the configuration of the studied system and degree of chain fluorination.

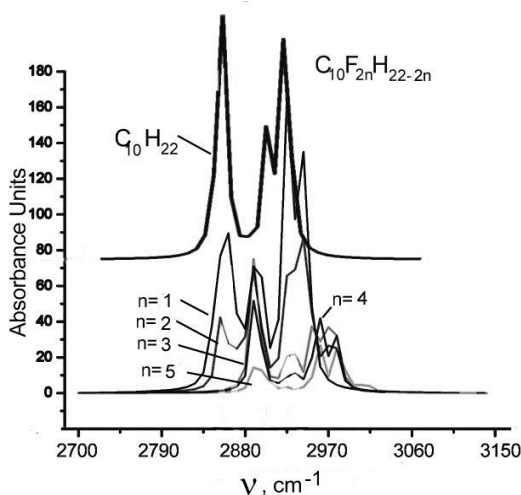


Fig.1. Calculated IR spectra of model molecules: $C_{10}H_{22}$ and $C_{10}F_{2n}H_{22-2n}$

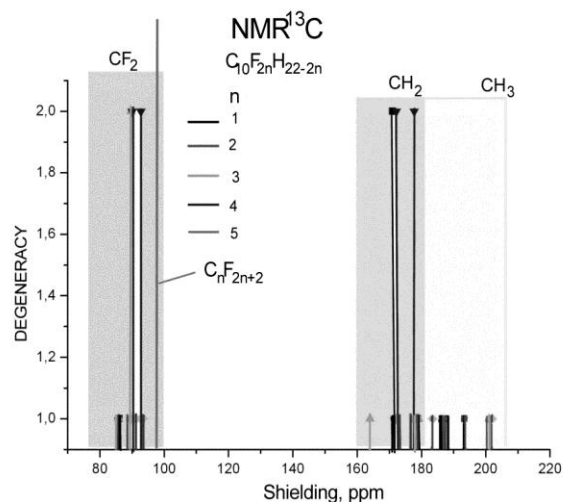


Fig.2. NMR¹³C spectra of model molecules: C_nF_{2n+2} and $C_{10}F_{2n}$

Fluoroalkyl End-Capped Oligomers/Polyaniline and /Phenyl-Capped Aniline Dimer Nanocomposites: Controlling Photochromism between These Nanocomposites Induced by UV-Light-Responsive Titanium Oxide Nanoparticles

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Polyaniline (**PAn**)/inorganic composites have been considered as new class of materials due to their improved properties compared with those of pure conducting polymers and inorganic materials. For example, the combination of electrical conductivity of **PAn** and UV sensitivity of anatase TiO₂ are expected to find applications in electrochromic devices, nonlinear optical system, and photochemical devices.¹ It is in general difficult to prepare conducting polymers/inorganic nanoparticle composites by conventional blending or mixing in solutions or melt form, because, polymers are not molten in nature and generally insoluble in common solvents.² On the other hand, partially fluoroalkylated polymers, especially fluoroalkyl end-capped oligomers are attractive polymeric surfactants, because they exhibit various unique properties such as high solubility, surface active properties, biological activities and nanometer size-controlled molecular aggregates which cannot be achieved by the corresponding non-fluorinated and randomly fluoroalkylated ones.³ Therefore, it is in particular interest to develop novel fluoroalkyl end-capped oligomers/**PAn** nanocomposites, especially fluoroalkyl end-capped oligomers/**PAn**/titanium oxide nanoparticles composites have high potential applications imparted by not only fluorine but also **PAn** or titanium oxide toward a variety of areas such as conductive coating, charge storage, electrocatalyst, electrochromic devices, and photovoltaic cells.

Here we report that fluoroalkyl end-capped acrylic acid oligomer [R_F-(ACA)_n-R_F]/, 2-methacryloyloxyethanesulfonic acid oligomer [R_F-(MES)_n-R_F]/, 2-acrylamido-2-methylpropanesulfonic acid oligomer [R_F-(AMPS)_n-R_F] /polyaniline [**PAn**]

nanocomposites are prepared by the polymerization of aniline initiated by ammonium persulfate in the presence of the corresponding oligomers, respectively. These fluorinated oligomers were also applied to the preparation of the corresponding fluorinated oligomers/phenyl-capped aniline dimer (**An-dimer**: *N,N'*-diphenyl-1,4-diphenyldiamine) nanocomposites by the interaction of the fluorinated oligomers with **An-dimer**, which is considered to be an excellent model of **PAn**. In these nanocomposites, R_F-(MES)_n-R_F/**PAn** nanocomposites and R_F-(MES)_n-R_F/**An-dimer** nanocomposites were effective for the preparation of colloidal stable fluorinated oligomer/**PAn**/TiO₂ and /**An-dimer**/TiO₂ nanocomposites. These two types of fluorinated TiO₂ nanocomposites can exhibit quite different photochromic behaviors: R_F-(MES)_n-R_F/**PAn**/TiO₂ nanocomposites can exhibit a reversible wavelength change for polaron absorptions around 760 ~ 820 nm by alternation of UV-irradiation and storage in the dark; in contrast, R_F-(MES)_n-R_F/**An-dimer**/TiO₂ nanocomposites can exhibit a reversible color change from blue to colorless (a reversible absorbance change) by the similar treatment.

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Optical and electrochemical properties of temperature fractions of nanodispersed polytetrafluoroethylene Forum®

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The original thermo-gas-dynamic (TGD) method of nanofluoropolymers (Forum®) synthesis based on the thermal destruction of bulk polytetrafluoroethylene (PTFE) under special gas-dynamic conditions was developed in the Institute of Chemistry FEBRAS [1]. PTFE FORUM® is the material consisting of polymer molecules of various molecular weights (Fig. 1).

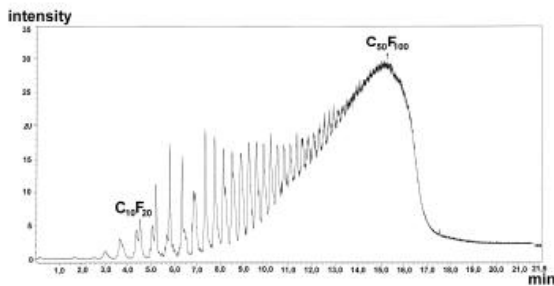


Fig. 1. Chromatography-mass spectrometry of PTFE low-molecular phase up to 400° C. At the temperature up to 400° C the molecules with molecular weights from 338 to 3000 transfer into the gas phase. Heating FORUM® powder in the defined temperature ranges allows generating fractions with defined molecular weights. Researches show that these fractions have different physical-chemical properties of practical interest. For example, film which is transparent in the optical band and generated from the PTFE FORUM® powder is able to absorb ultraviolet radiation. The degree of absorption is inversely proportional to the fraction's molecular weight (Fig. 2).

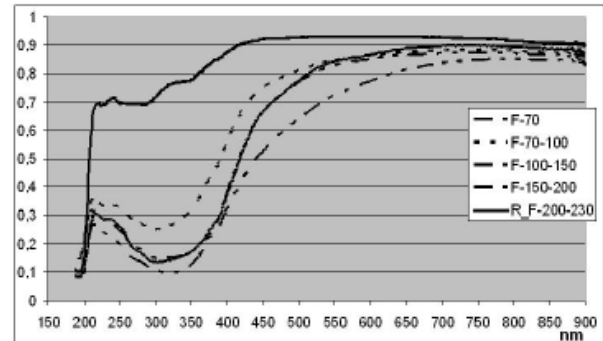


Fig. 2. Experimental light-spectrums of PTFE Forum® temperature fractions' reflection.

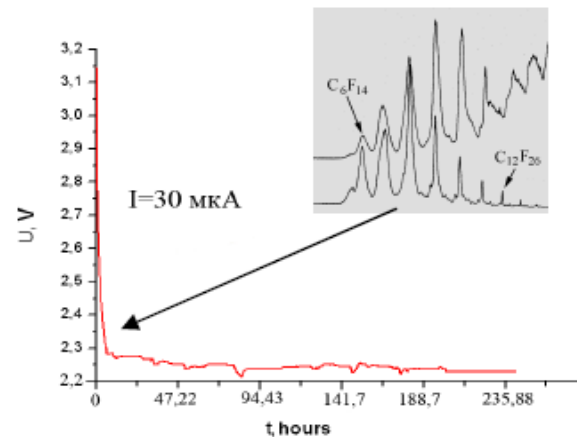
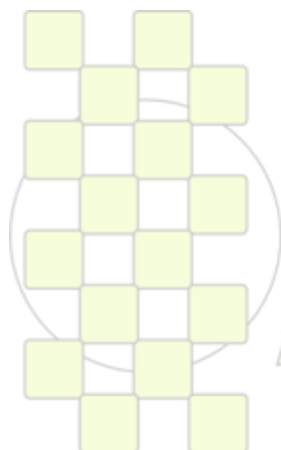


Fig. 2. The LCB discharge curve on the C₈F₁₆ cathode

This paper contains the results of physical-chemical, structural and morphological researches of different PTFE FORUM® temperature fractions.

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PVDF/Copper Nanocomposites: Preparation and Properties

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Introduction

The insertion of nanometric inorganic compounds in polymeric matrices provides an interesting method to improve some polymers properties, such as electric, thermal, optic or the magnetic ones. On the other hand the resulting materials present the advantages from polymers regarding processability¹, flexibility or less weight and price in comparison with traditional metals. The nanometric structure sometimes shows properties different from those of the same material in a higher level structure^{2,3}. For example, polymer composites with conductive metallic particles can be used as antistatic or in electromagnetic interference shielding applications⁴. As a result, this methodology has a lot of applications depending upon the inorganic material incorporated within the polymers.

Materials and Methods

Composites of poly(vinylidene fluoride), PVDF, with copper nanoparticles (with a nominal average particle size of 25 nm) have been prepared at different compositions via melt blending. The films obtained were characterized from a morphological and thermal standpoint by transmission and scanning electron microscopies, synchrotron radiation, thermogravimetry and differential scanning calorimetry. Synchrotron X-ray measurements were performed at the CRG beamline BM16 of the ESRF (Grenoble, France). In addition, the molecular dynamic and mechanical properties of the samples have been evaluated.

Results and Discussion

Scanning electron micrographs of cryofractured specimens show a homogeneous dispersion of copper nanoparticles within the polymer matrix without significant aggregation. An increase in the mechanical parameters related to rigidity, such as young modulus or microhardness, is found when the content of metal does. However, an opposite effect is observed for the properties related to the deformation of the polymer.

The effectiveness of a shield and its resulting electromagnetic interference attenuation depend on the frequency, the distance of the shield from the source, the thickness of the shield, and the shield material. In the present samples, shielding effectiveness is expressed as a function of the ratio of the incident and transmitted X-ray radiation (with a wavelength of 0.098 nm). Figure 1 shows a decrease in more than four orders of magnitude of the incident electromagnetic radiation when the sample with 20 vol% copper is used as shield.

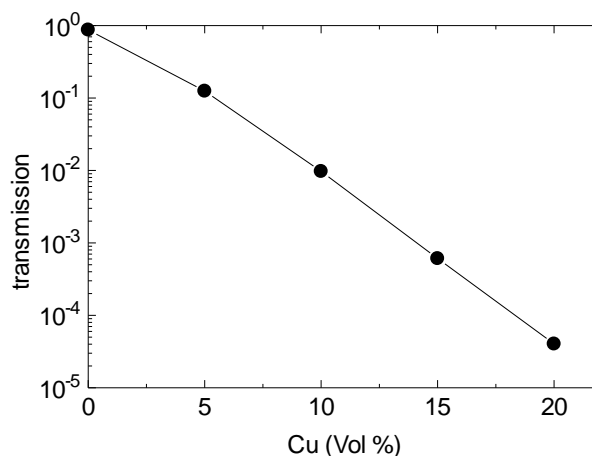


Figure 1. Normalized transmission of X-ray radiation as a function of Cu content in the PVDF/copper nanocomposites.

Conclusions

The dependence of different physical properties on copper nanoparticles concentration has been studied for poly(vinylidene fluoride) nanocomposites. A good distribution of nanoparticles is observed in these PVDF-based materials independently of their composition. On the other hand, a significant improvement is found in some of the properties evaluated.

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Acknowledgements

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J. Arranz-Andrés thanks to the CSIC JAE-Doc Program for his financial support.

Fluorinated epoxy resin nanocomposites reinforced with amine functionalized MWNTs

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Introduction: Nanosized fillers such as carbon nanotubes, clay and nanofibers have been considered suitable reinforcing materials for epoxy resins to produce high performance composites with enhanced properties. Carbon nanotubes (CNTs) are excellent candidates for improvement of thermo-mechanical properties of epoxy resins [1]. Raw CNTs have a tendency to aggregate because of their large surface area and strong resultant van der Waals forces. The dispersion of CNTs is very important in order to fully realize improvement in epoxy based CNT composites, this being improved considerably by functionalization [2] Aiming the enhancement of the dielectric properties and the moisture resistance of classic DGEBA epoxy resins, the present research proposes fluorinated epoxy nanocomposite systems reinforced with amine modified Multiwalled Carbon Nanotubes (MWNT).

Materials and methods: Fluorinated epoxy resin was synthesized from epichlorohydrine and 4,4'-(Hexafluoroisopropylidene)diphenol by a method described in the literature [3]. Amine modified nanotubes have been obtained by a two step reaction: first step is the interaction between carboxylated MWNTs and thionyl chloride ($SOCl_2$) to obtain acylated groups on the nanotubes surface, second step was the interaction between acylated MWNTs and the amines modifying agents: benzylamine (BA) and a polyetheramine (B100). Functionalization was proved by TGA, FT-IR, XPS and SEM analysis. The modified CNTs were dispersed in diglycidylether of hexafluorinated bisphenol A (DGEFBA) by tip sonication, cured with an aromatic polyamine (Poly(m-xylylenediamine-alt-epichlorohydrin) diamine terminated) by a two step temperature schedule to obtain the final composites. Composite samples were characterised by TGA, DMA, DSC and SEM analysis.

Results and discussion: XPS surface characterization of functionalized MWNTs showed a decrease of the oxygen content for MWNT-BA and subsequent appearance of nitrogen bonds from the amine groups. Amine groups were present also in the MWNT-B100, but due to the ether groups from the B100 backbone, the O1s content was slightly increased as shown in table 1.

Table 1 XPS data for functionalized MWNTs

Nanotubes Type	At. C1s %	At. O1s %	At. N1s %
MWNT-COOH	83.8	16.2	0
MWNT-BA	88.3	9.7	2.0
MWNT-B100	81.8	16.9	1.3

Thermostability of the DGEFBA composites systems, defined as the temperature of 3% weight loss ($Td_{3\%}$), was obtained using TGA technique. Compared with the neat DGEFBA, the composites reinforced with only 0.3% of functionalized MWNTs showed a $\sim 20^\circ\text{C}$ improvement of $Td_{3\%}$ (figure 1), meaning that the epoxy network was

strengthened by the one formed through the good dispersion of the nanotubes.

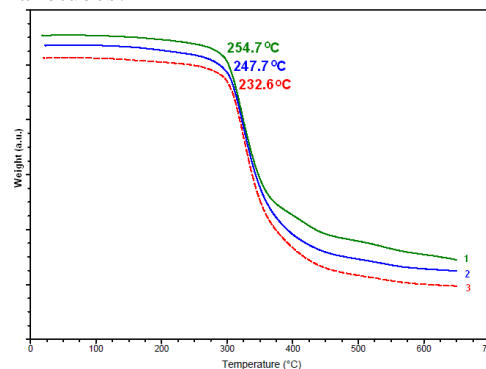


Fig. 1 TGA curves of 1) DGEFBA/MWNT-B100
2) DGEFBA/MWNT-BA; 3) neat DGEFBA;

The curing process of the initial composite systems was studied by dynamic DSC, resulting that 0.3% of functionalized MWNTs do not affect significantly the reaction enthalpy (~ 290 J/g) and the maximum cure temperature ($\sim 99^\circ\text{C}$).

Fluorinated epoxy resins are known as hydrophobic materials with high resistance to the moisture environment. Due to this fact it was noticed a low compatibility with the carboxylic groups from the MWNTs surface resulting in agglomerates. The SEM images for amine functionalized MWNTs (Fig.2.B) showed well dispersed nanotubes in the DGEFBA resin, which is responsible for the enhancement of the new composites.

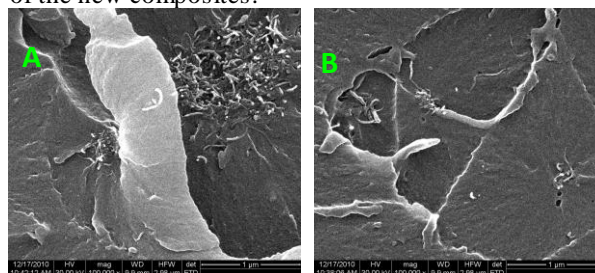


Fig. 2 SEM images of DGEFBA composites with
A) MWNT-COOH and B) MWNT-B100

Conclusions: MWNTs were functionalized with two aromatic amines in order to improve their compatibility with fluorinated epoxy resin. The new composites showed improved thermal stability and good dispersion.

Acknowledgments: This work was kindly supported by CNCIS – UEFISCSU through project number PNII – IDEI 1718/2008

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Fluorescent Polynorbornene/Oxazine-1 Loaded Fluoromica Nanocomposites by *In Situ* Polymerization for Solution Processable Electronics

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In the growing world of nanotechnologies, a particular interest has been given to the synthesis of hybrid supramolecular assemblies, arranged into ordered nano-scaled architectures embedding photofunctional dyes, for the development of optoelectronic devices. [1]

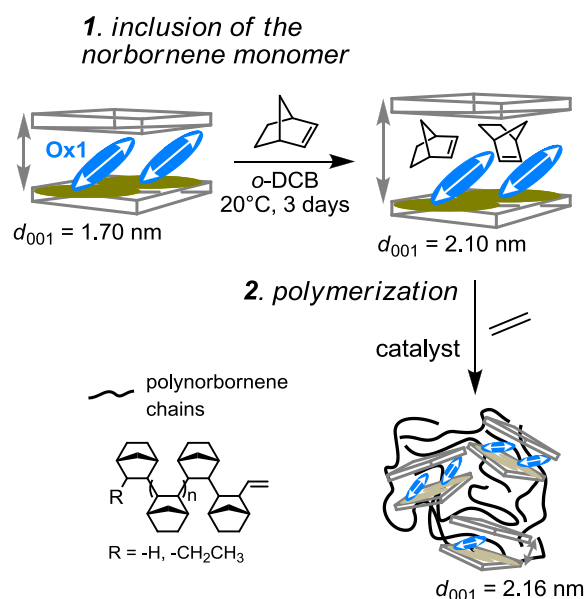
A common limitation of organic dyes is their susceptibility to chemical and photochemical degradation. Moreover, their tendency to aggregate induces multichromophoric interactions that alter the color quality and give unfavorable non-fluorescent species. In order to overcome these drawbacks, many researchers began investigating hybridization of the dye by addressing these molecules into different organic or inorganic hosts. Among host-guest assemblies, layered silicates belonging to the family of 2:1 phyllosilicate clays have proved to be very convenient hosts, especially because they offer unique two-dimensional expandable interlayer spacing to yield organized intercalated guest species. [2] To date, several luminous dye-clays have been extensively studied to prepare functional assemblies. However, the fabrication of optoelectronic devices with these hybrids is still a challenging task because of the still poor film quality.

We thought that a possible way to find a solution to the above critical points could have been the incorporation of dye doped clays into a flexible polymeric matrix, allowing to maintain the dye luminescence properties and to improve the film processability at the same time.

Following this idea, we have now prepared fluorescent polynorbornene/oxazine-1 (Ox1) loaded fluoromica nanocomposites by *in situ* polymerization via Ziegler-Natta catalysis.

Sodium-fluoromica is modified with cationic Ox1 dye by ion-exchange: at higher Ox1 loading the dye adopts a much more perpendicular orientation of the long-molecular axis with respect to the clay layer surface. As a result of this tilted geometrical arrangement the clay *d*-spacing increases and minimizes the area covered per a monolayer intercalated Ox1 molecules. These features facilitate the entry of the incoming polymerizable monomers (*i.e.*, norbornene and ethylene) in between the clay galleries, and thus the interlayer growth of the macromolecular chains (see Scheme 1). [3] When the polymerization is initiated within the layers, where the slabs of the inorganic host act as a template, an ordered and well-dispersed multicomponent polymeric hybrid, in which dyes are highly oriented in the inorganic framework, is formed. Nanocomposites exhibit an improved solubility with respect to the dye/clay compounds, which made the polynorbornene composite easy processable by spin-coating technique. Absorption and photoluminescence

studies show that the nanohybrids exhibit the presence of dye species having features of both Ox1 monomer molecules and J-dimers.



Scheme 1.

The nanocomposites show four main advantages: (i) a high dye concentration can be achieved avoiding non-fluorescent dye aggregate formation; (ii) the clay aggregation is hampered by the polymer chains that wrap the clay platelets; (iii) the solubility is improved with respect to the dye/clay compounds, making the polymer composites easy processable by spin-coating technique; (iv) the presence of the hydrophobic poorly-polar polymer in between the clay layers affords a phase segregation which drives the dye molecules to adopt less conformational degrees of freedom until to increase the head-to-tail interaction (J-aggregates) between them.

In conclusion, the results obtained open up unprecedented prospects for the synthesis of novel luminescent polymer hybrids which can be used to fabricate functional devices with unique photoluminescence properties.

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Characterization of different varieties of cassava flour by solid state NMR spectroscopy

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Introduction

Cassava (*Manihot esculenta Crantz*), known in Brazil as “mandioca”, “macaxeira” or “aipim”, is the main crop cultivated in several farming in Brazil and, also, in other areas in tropical América [1]. Cassava flour is mainly constitutes by starch, fiber, proteins, lipids and minerals [2,3]. However, it is known that the percentage of these components may differ substantially between the varieties, resulting in differences in their nutritional aspect. The focus of this paper was to investigate six varieties of cassava with respect to chemical composition and molecular dynamic behavior, employing nuclear magnetic resonance spectroscopy (NMR).

Materials and Methods

The samples were characterized by different solid-state NMR techniques, such as cross polarization magic-angle spinning (CPMAS), variable contact time (VCT), and proton spin-lattice relaxation time in the rotating frame ($T_{1\rho H}$). The ^{13}C NMR spectra were obtained on a Varian INOVA 300 spectrometer operating at 75.4 MHz for ^{13}C . For the VCT experiment, a range of contact time was established from 200 to 8,000 μs , and $T_{1\rho}$ values were determined from the intensity decay of ^{13}C peaks with increasing contact times.

Results and Discussion

^{13}C CPMAS NMR spectra (Fig. 1) showed three NMR signal located in a particular region that is assigned as polysaccharides, indicating that these samples consist mainly of starch. Comparing the ^{13}C CPMAS spectra of M1, M2 and M3 cassava samples they present a different structural organization in relation to the other samples, since NMR signals are located at lower chemical shifts, suggesting that those samples are more amorphous, probably due to the higher quantity of amylose ratio in starch composition.

From VCT experiment (Fig 2), it was observed a simple decay for all resolved ^{13}C signals. This molecular behavior shows that these samples have molecular rigidity. The best contact-time for the polarization transfer between ^1H and ^{13}C was 800 μs for all cassava flour samples, excluding M1 in which 400 μs was detected as a best contact-time. This result shows that M1 sample is more rigid than the others, due to its stronger intermolecular interactions, indicating that M1 sample probably has differences in its chemical composition.

The VCT experiment permits us to determine the $T_{1\rho H}$ relaxation time (Table 1). It can be seen that M2, M3, M4 and M6 samples are more homogeneous, since $T_{1\rho H}$ values are more uniform, while M1 and M5 samples show some heterogeneity in their composition and/or molecular organization. It was also observed, that M4 sample present a slightly lower molecular mobility. The $T_{1\rho H}$ behavior is related to chains interaction/proximity,

which may be understood as indicating that M4 sample have higher amylopectin proportion, since this component is responsible for the crystallinity in starch granules [4].

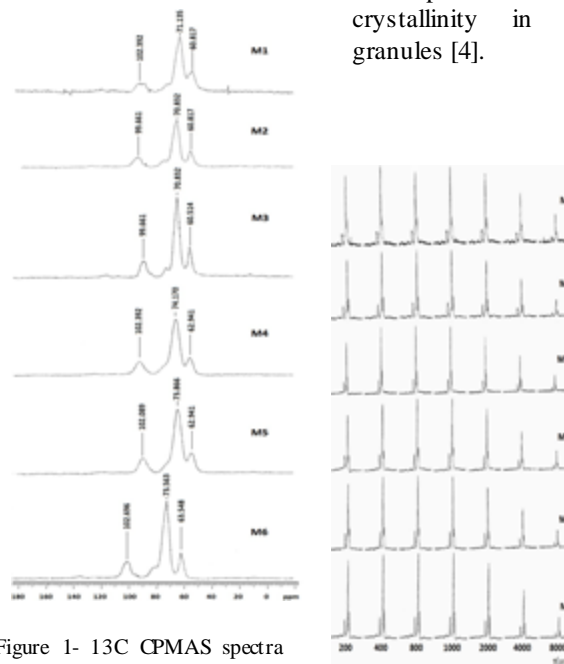


Figure 1- ^{13}C CPMAS spectra for

Figure2- VCT experiment

Table 1 - Proton spin-lattice relaxation parameter from cassava samples, determined during the VCT experiment

	Cassava Samples					
	M1	M2	M3	M4	M5	M6
$\delta(\text{ppm})$	102	99	100	102	102	103
	71	71	71	74	74	74
	60	61	61	63	63	64
$T_{1\rho H}$ (ms)	4	4	6	3	4	5
	11	6	5	3	6	5
	13	6	7	3	11	6

Conclusions

Solid state NMR techniques provided important information on chemical and structural characteristics of different cassava varieties. From the NMR data obtained in this study, it appears that the cassava samples studied showed variations on nutritional aspects based on their molecular structure and chemical composition, serving as markers for specific diets.

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Characterization of Conducting Polymer Nanocomposites with Poly(vinylidene fluoride) Used in Devices Electroluminescents

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Introduction: It is well known the concern of scientists in producing devices for conversion and clean power generation. Among the devices studied stand out the organic light emitting diodes (OLEDs), the polymer light emitting diodes (PLEDs) and light emitting devices based in luminophors components. The efficiency of these devices has increased in recent years; however, more studies should be conducted to enlarge it. This paper presents the construction and characterization of components of an electroluminescent device consisting of: Monolayers of composites of various thicknesses (4 μm -20 nm) containing poly (3-thiophene methyl acetate) PT3MA doped with ferric chloride (FeCl_3), the polymer poly (vinylidene fluoride) and the luminophor $\text{ZnSiO}_4:\text{Mn}$ (zinc silicate doped with manganese), which were dissolved in dimethylformamide (DMFA) and deposited by spinner or drop casting techniques on Indium Titanium Oxide (ITO) and silicon wafers. The film formed was then taken to evaporation of metals and in its opposite face deposited aluminum to form external contacts. The samples were characterized with the techniques of atomic force microscopy (AFM), focused ion beam (FIB) scanning electron microscopy, ellipsometry, perfilometry and I-V characteristic curve.

Materials and Methods

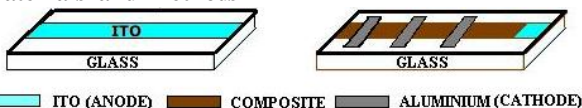


Figure 1: Device fabrication process

The steps for assembling and preparing the device (Figure 1) are: 1) partial removal of the ITO by corrosion process using Zn powder and HCl 1:1¹, 2) clean of substrate with solvents (acetone, water and isopropyl alcohol using ultrasound)¹, 3) deposition of the composite by drop casting or spinner, 4) evaporation of the solvent in the vacuum oven, 5) deposition of aluminum by sputtering with the aid of mask

Results and discussion: The average thickness determined by Perfilometry and FIB to the composite deposited on the substrate by drop casting was 4 μm . In the tests evidence of depositions by spinner, nanocomposites of the material can be obtained and their values of thicknesses determined by ellipsometry. The solutions spin coated at 1000 rpm and 2000 rpm formed membranes with thicknesses near 20 nm. The SEM images showed an excellent distribution of luminophors in the films thicker, however low their distribution in the nanocomposites deposited by spinner

resulting in an increase of the agglomeration of luminophors particles in the extremities of the ITO surface.

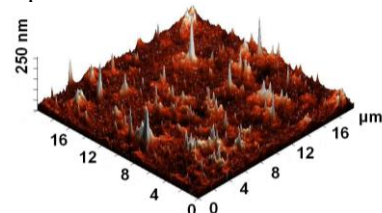


Figure 2: AFM images of nanocomposite
AFM images were performed to determine quantitatively the average roughness of the composites deposited on the substrates. Figure 2 shows the surface topography of the composite deposited on ITO substrate by spinner at 2000 rpm with a value of average roughness of 11 nm. Composites with values of 450 nm and 14 nm of roughness were obtained respectively by drop casting and spinner at 1000 rpm. The I-V characteristic curve of composite PT3MA / PVDF / $\text{ZnSiO}_4:\text{Mn}$ with 2 μm of thickness and 0,3 cm^2 of area is presented in Figure 3. The measurements were performed for a sample polarized with direct current (DC) voltage using a slope of 93 mV/dec.

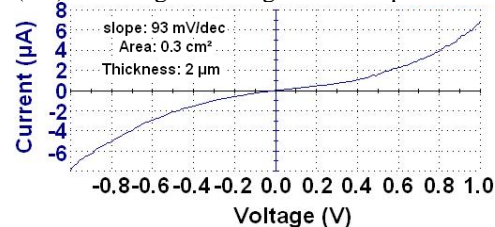


Figure 3: I-V characteristic curve voltage x current
Analyzing the curve is possible to observe that the device presents a behavior characteristic of a semiconductor diode. However for voltages greater than 3 volts a new behavior is observed, because the curves show the formation of hysteresis (graph not reported in this paper). These results are similar to those reported for blends of PVDF-PT3MA².

Conclusion: The films obtained this work presented low roughness, excellent distribution of luminophors, especially the thicker films. The electrical characteristic voltage versus current (VxI) showed a diode behavior and not resistive for the device.

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Characterization of different varieties of cassava flour by solid state NMR spectroscopy

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Introduction

Cassava (*Manihot esculenta Crantz*), known in Brazil as “mandioca”, “macaxeira” or “aipim”, is the main crop cultivated in several farming in Brazil and, also, in other areas in tropical América [1]. Cassava flour is mainly constitutes by starch, fiber, proteins, lipids and minerals [2,3]. However, it is known that the percentage of these components may differ substantially between the varieties, resulting in differences in their nutritional aspect. The focus of this paper was to investigate six varieties of cassava with respect to chemical composition and molecular dynamic behavior, employing nuclear magnetic resonance spectroscopy (NMR).

Materials and Methods

The samples were characterized by different solid-state NMR techniques, such as cross polarization magic-angle spinning (CPMAS), variable contact time (VCT), and proton spin-lattice relaxation time in the rotating frame ($T_{1\rho H}$). The ^{13}C NMR spectra were obtained on a Varian INOVA 300 spectrometer operating at 75.4 MHz for ^{13}C . For the VCT experiment, a range of contact time was established from 200 to 8,000 μs , and $T_{1\rho}$ values were determined from the intensity decay of ^{13}C peaks with increasing contact times.

Results and Discussion

^{13}C CPMAS NMR spectra (Fig. 1) showed three NMR signal located in a particular region that is assigned as polysaccharides, indicating that these samples consist mainly of starch. Comparing the ^{13}C CPMAS spectra of M1, M2 and M3 cassava samples they present a different structural organization in relation to the other samples, since NMR signals are located at lower chemical shifts, suggesting that those samples are more amorphous, probably due to the higher quantity of amylose ratio in starch composition.

From VCT experiment (Fig 2), it was observed a simple decay for all resolved ^{13}C signals. This molecular behavior shows that these samples have molecular rigidity. The best contact-time for the polarization transfer between ^1H and ^{13}C was 800 μs for all cassava flour samples, excluding M1 in which 400 μs was detected as a best contact-time. This result shows that M1 sample is more rigid than the others, due to its stronger intermolecular interactions, indicating that M1 sample probably has differences in its chemical composition.

The VCT experiment permits us to determine the $T_{1\rho H}$ relaxation time (Table 1). It can be seen that M2, M3, M4 and M6 samples are more homogeneous, since $T_{1\rho H}$ values are more uniform, while M1 and M5 samples show some heterogeneity in their composition and/or molecular organization. It was also observed, that M4 sample present a slightly lower molecular mobility. The $T_{1\rho H}$ behavior is related to chains interaction/proximity,

which may be understood as indicating that M4 sample have higher amylopectin proportion, since this component is responsible for the crystallinity in starch granules [4].

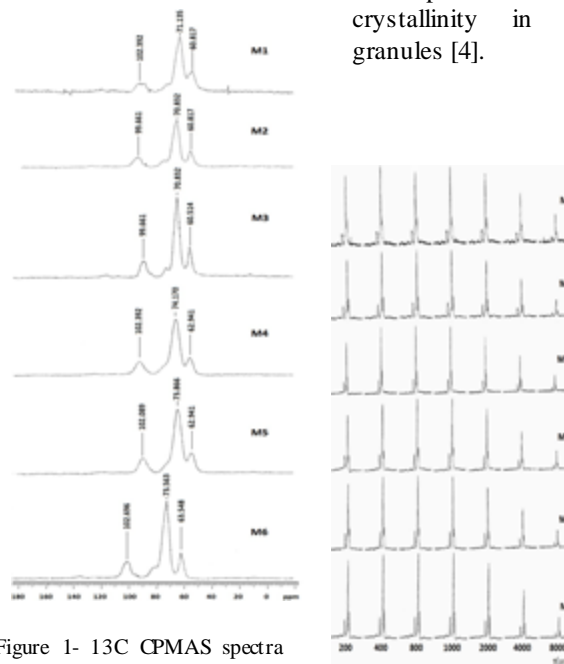


Figure 1- ^{13}C CPMAS spectra for

Figure2- VCT experiment

Table 1. Proton spin-lattice relaxation parameter from cassava samples, determined during the VCT experiment

	Cassava Samples					
	M1	M2	M3	M4	M5	M6
$\delta(\text{ppm})$	102	99	100	102	102	103
	71	71	71	74	74	74
	60	61	61	63	63	64
$T_{1\rho H}$ (ms)	4	4	6	3	4	5
	11	6	5	3	6	5
	13	6	7	3	11	6

Conclusions

Solid state NMR techniques provided important information on chemical and structural characteristics of different cassava varieties. From the NMR data obtained in this study, it appears that the cassava samples studied showed variations on nutritional aspects based on their molecular structure and chemical composition, serving as markers for specific diets.

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Fluorene-Derivative Containing Polymers as Sensory Materials for the Colorimetric and Fluorogenic Sensing of Analytes.

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Introduction

Due to the outstanding mechanical properties of aromatic polyamides (aramids), we have used the aramid backbone to prepare advanced functional materials. Thus, we have synthesized chemically modified copolyamide consisting of 90% of structural units of poly(*m*-phenylene isophthalamide) (NOMEX[®]) and 10% of structural units containing pendant fluorene

derivatives. Following this strategy, the excellent mechanical and thermal properties of NOMEX[®] were maintained, and the materials gave rise to creasable films or dense membranes to be used as colorimetric or fluorescence sensory materials.¹ Moreover, a 10% mole content of the structural units with the urea binding site and fluorescent fluorene group is especially adequate for measuring changes in the fluorescence behavior upon interaction with analytes and, sufficient for giving rise to perceptible “naked eye” colorimetric variations.

Results and discussion

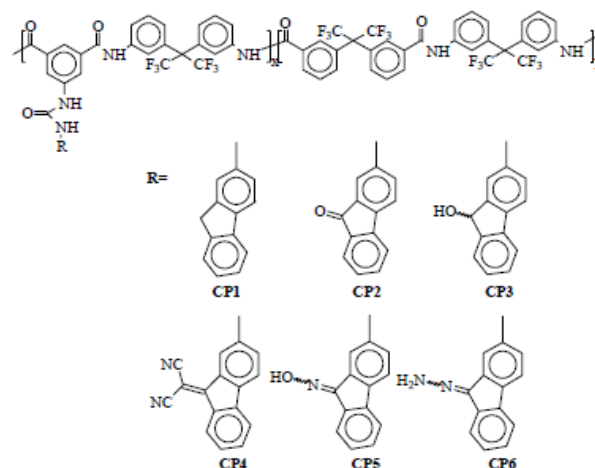
The copolymer **CP1** was firstly prepared and then chemically modified to render copolymers **CP2** to **CP6** (Scheme 1).² These modifications were carried out following orthogonal and high yielding reactions and were previously studied using model compounds. This synthetic approach has proven to be a really adequate strategy to prepare new functional soft materials. The reaction conditions were optimized with the model compounds and then applied to the polymers. These model compounds were also used to study the chromogenic and fluorogenic behaviour of the polymers in solution, supposing that each model mimics the behaviour of its corresponding polymer, but with a defined molecular weight and higher solubility.^{3,4}

Chromogenic and fluorescence behavior

As previously outlined, the chromogenic and fluorescent behaviors of high-performance polymers are key properties for many novel applications, such as for chromogenic and fluorogenic sensing materials or for hybrid LUCO/LED emitting devices. The copolymers (Scheme 1) give rise to fluorescent and colored solutions in organic solvents. Upon addition of different anions, a fluorogenic and chromogenic response is observed, as depicted for CP2 in Figures 1 and 2. Thus, the addition of CO₃²⁻ gives rise to a selective color change and to the fluorescence quenching.

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Scheme 1. Chemical structure and codes of the modified copolyamides.

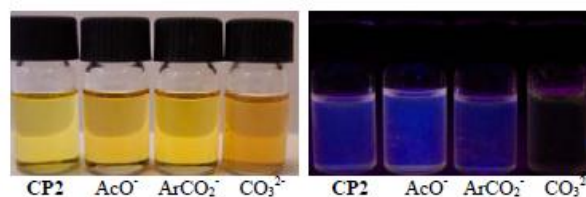


Figure 1. Chromogenic (left) and fluorescence (right) images of solutions of copolyamide **CP1**, **CP2**, **CP3**, **CP4**, **CP5** and **CP6** (from left to right) in DMSO ($8 \times 10^{-3} \text{M}$). The anions have a concentration of $2 \times 10^{-2} \text{M}$. The right photograph was taken under irradiation with UV (365nm).

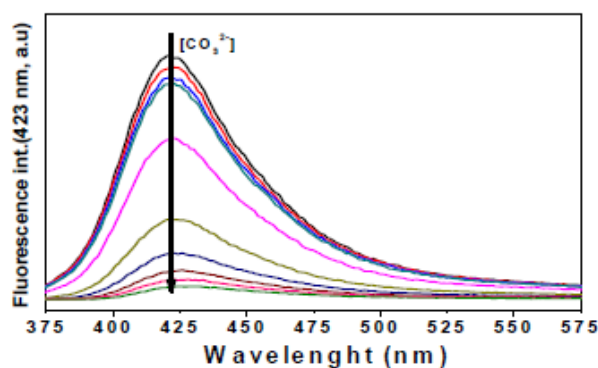


Figure 2. Fluorescence titration curves of a DMSO solution of the copolyamide **CP2** with potassium carbonate (fluorescence intensity at 423 nm).