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Treball Final de Grau

Preparation of fluorescent polymeric microparticles based on 9-vinylcarbazole.

Preparació de micropàrticules d'un polímer fluorescent basat en el 9-vinilcarbazol.

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Nothing in life is to be feared, it is only to be understood. Now is the time to understand more, so that we may fear less.

Marie Curie

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REPORT

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1. SUMMARY

Plastic scintillation technique is a method for determining mainly beta emitting radionuclides, but also alpha, which has some advantages over liquid scintillation, the most commonly used technique. Some of the main advantages of plastic scintillation is that it avoids the generation of mixed waste and offers the possibility of a selective radionuclide determination in a complex sample using a selective extractant (PSresin).

Plastic scintillation measurements are based on the preparation of polymer microspheres that contain fluorescent molecules (PSm). The synthesis of PSresin requires, in some cases, the creation of covalent bonds between the extractant and the microspheres. Sometimes, during the synthesis of this type of PSresin, the fluorescent molecules are solubilized and lost.

In this work, it has been studied the possibility of using a polymerizable fluorescent molecule, 9-vinylcarbazole, which may enable doing the scintillation measurements with no specific fluorescent molecules. Because of this, poly(9-vinylcarbazole) has been synthesized and its scintillation capabilities have been evaluated as: whole scintillator system, mixed with polystyrene and copolymerized also with polystyrene.

The results conclude that PSm of copolymer synthesized from styrene and 9-vinylcarbazole (90:10) are the ones that offer the most promising results reaching a detection efficiency values of 30% for ^{14}C , 155% for ^{90}Sr / ^{90}Y and 84% for ^{241}Am .

Keywords: plastic scintillation, liquid scintillation, radioactivity, 9-vinylcarbazole, poly(9-vinylcarbazole), PVK, PSm, PSresin.

2. RESUM

La tècnica de centelleig plàstic és un mètode de determinació de radionúclids emissors de partícules principalment beta, però també alfa, que presenta alguns avantatges sobre el centelleig líquid, la tècnica habitualment més utilitzada. Alguns dels principals avantatges del centelleig plàstic és que evita la generació de residus mixtes i que ofereix la possibilitat de dur a terme la determinació selectiva d'un radionúclid en una mostra complexa per mitjà de l'ús d'un extractant selectiu (PSresin).

Les mesures per centelleig plàstic es basen en la preparació de microesferes de polímer que contenen molècules fluorescents (PSm). La síntesi de PSresin, en alguns casos, requereix la creació d'enllaços covalents entre l'extractant i les microesferes. En ocasions, durant la síntesi d'aquest tipus de PSresin, les molècules fluorescents es solubilitzen i es perden.

En aquest treball s'ha estudiat la possibilitat de fer servir una molècula fluorescent polimeritzable, el 9-vinilcarbazol, que permeti prescindir de les molècules fluorescents per fer les mesures de centelleig. Per això, s'ha sintetitzat el poli(9-vinilcarbazol) i s'ha avaluat les seves capacitats de centelleig pur, en una barreja de polímers amb poliestirè i copolimeritzat també amb poliestirè.

Els resultats conclouen que les PSm de copolímer sintetitzat a partir d'estirè i 9-vinilcarbazol (90:10) són les que ofereixen uns resultats més prometedors arribant a assolir uns valors d'eficiència de detecció del 30% per ^{14}C , 155% per $^{90}\text{Sr}/^{90}\text{Y}$ i 84% per ^{241}Am .

Paraules clau: centelleig plàstic, centelleig líquid, radioactivitat, 9-vinilcarbazol, poli(9-vinilcarbazol), PVK, PSm, PSresin.

3. INTRODUCTION

3.1. RADIOACTIVITY

Radiations can be classified as ionizing and non-ionizing depending on their capacity to ionize matter or not. Non-ionizing radiations, like microwaves, radiofrequency waves or visible light, have low energy and, in general, are less dangerous, but ionizing radiations can produce easily damages to human health for their capability to ionize molecules or atoms of the medium. Ionizing radiations include radioactive emissions.

Radioactivity is the process where an unstable atom emits energy in form of nuclear particles and electromagnetic radiation, and it is transformed to another element with more stability. Depending on the nature of these emissions, can be classified as: alpha particles, beta particles and gamma radiation. Each one has different characteristics and properties as it will be explained later.

Radioactive elements can be found in many different places. Every day we interact with many potential focuses of radioactivity without knowing it. Must be said that the major part corresponds to low activities, so the received doses are inoffensive for people's health. In addition, it is generally though that radioactivity is something artificial, created by human being, but is something also natural that has always existed in nature. Radioactive elements such as uranium-235, uranium-238, thorium-229, radon-222, potassium-40 or carbon-14 can be found in the environment. Some of them, like ^{14}C or ^{40}K , can be found in human body and, together with cosmic radiation, are responsible of most of the dose received by humans. As a curiosity, ^{40}K is the most abundant radionuclide present in human body with an estimated activity of about 4,500 Bq for a 70 Kg human body [1].

Radioactivity, from natural or artificial origin, is present in many different type of activities thanks to its multiple uses. It can be used in many industries, for medical purposes or in research activities. For example: nuclear power plants use radioactivity to produce electric energy through nuclear fission reactions and, in medicine, ionizing radiations from radioactive emissions are used

for radiodiagnosis and radiotherapy. All these activities usually need accurate radioactivity detection techniques to be performed.

On the other hand, many of these activities produce radioactive wastes which must be stored or discharged if its activity is low enough. At any case, there is a necessity to perform monitoring of the environment to control discharges and detect illegal spills or accidents. Also, terrorism acts with radioactive effects could be a contamination focus that must be taken into account. Therefore, detection techniques are essential to measure radioactivity levels in the environment in order to prevent people's health and the environment itself from the danger of ionizing radiations.

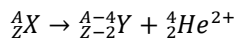
3.1.1. Radioactive emissions

The radioactive emissions can be classified as alpha and beta particles and gamma radiation. Each one has different characteristics and properties [2].

3.1.1.1. Alpha particles (α)

An alpha particle is a charged helium nucleus, so it consists of two protons bound with two neutrons. It has a considerable mass compared to other particle emissions like beta particles. Because of this, alpha particles have a low penetration power into matter but a high ionization capacity. This means that alpha particles can not pass through a tiny paper sheet or even through some centimeters of air due to the collisions with molecules like nitrogen or oxygen.

Alpha emitters are usually unstable atoms with a high atomic weight like uranium, americium plutonium or radon isotopes. The repulsions between their protons and neutrons are too high so they emit an alpha particle in order to decrease its size and achieve more stability as it is represented on the next expression:



In addition, alpha particles are usually accompanied by gamma radiation.

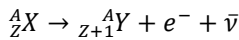
3.1.1.2. Beta particles (β)

A beta particle is an electron (if it has negative charge, β^-) or a positron (if it has a positive charge, β^+). It has a very low mass, so beta particles radiation has medium penetration power

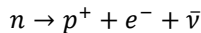
and ionization capacity. Unlike alpha particles, beta particles can pass through a sheet of paper and even penetrated some millimeters into skin but are stopped by some millimeters of aluminium.

Two different disintegrations can be described depending on the nature of beta particles emitted:

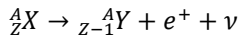
- β^- disintegration:



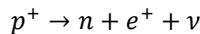
Where a neutron becomes a proton and emits an electron and an antineutrino:



- β^+ disintegration:



Where a proton becomes a neutron and emits a positron and a neutrino:

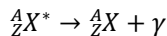


The most common beta emissions are produced by atoms with too many neutrons in their nucleus. When the ratio between neutrons and protons is too high, one of these neutrons decomposes into a proton and an electron (β^- disintegration). Some examples of beta emitting radionuclides are strontium-90, hydrogen-3 (tritium), carbon-14 or nickel-63.

Beta emissions are usually accompanied by gamma radiation, too.

3.1.1.3. Gamma radiation (γ)

Unlike alpha and beta, gamma rays are electromagnetic radiation. Because of this, gamma radiation has different characteristics to the other two types of radioactive emissions. After an alpha or beta decay, if the nucleus of the radionuclide is still excited, it can come back to the ground state emitting gamma radiation as it is represented on the next expression:



As high energy waves, gamma emissions have a high penetration power into matter but a very low ionization capacity. This high energy allows them to penetrate human skin and tissue and only very dense material such as lead can be used to stop or slow them. X-rays have same characteristics as gamma radiation only differentiated by their origin. Gamma rays are originated in the nucleus of the atom while X-rays come from the electron shell.

3.2. RADIOACTIVITY DETECTION: SCINTILLATION TECHNIQUE

Gamma rays are easily detected using gamma spectroscopy and alpha particles are also easily determined by alpha spectroscopy, although alpha determination has a complicated sample treatment procedure. Gamma and alpha emissions are monoenergetic, so the radionuclide emitter can be identified immediately by the energy of the emission detected.

However, determination of beta particles emitting radionuclides is more complicated. Beta particles are not monoenergetic, so all beta particles emitted from the same radionuclide have different energies from 0 to a maximum energy. Because of this, is difficult to identify them by a spectroscopy technique and several techniques for beta emitters determination have been developed.

We are going to focus on the main technique for beta emitting radionuclides determination which is scintillation technique. This technique can be also used for alpha emitting radionuclides determination.

It is called scintillation method because it is based on the idea of counting and classifying tiny flashes of light which are proportional to the amount of emissions (alpha or beta) emitted by a radionuclide. In scintillation techniques, the kinetic energy of the beta particle emitted is transformed to luminous energy because these flashes are, ultimately, the result of a fluorescence emission. The scintillator system is composed by a solvent with aromatic structure capable to catch the energy of the radioactive particle and a fluorescence substance which, later, transforms this energy into photons which are, finally, detected by the photomultiplier.

Two different types of scintillation technique can be differentiated: liquid scintillation and plastic scintillation. In liquid scintillation, the aromatic solvent is a liquid while in plastic scintillation the solvent is a polymer. In both cases, the scintillators (solvent and fluorescent substances) are mixed with the radioactive sample solution in a measuring vial. The differences and characteristics of each one will be explained in 3.2.2. and 3.2.3. sections.

The mechanism of scintillation is the same for liquid and plastic scintillation [2,3]:

1. The beta (or alpha) particle emitted by the radionuclide transfers a part of its energy to the substance used as solvent through the excitation of solvent molecules. The emitted particle can excite other solvent molecules before losing all its energy, so for every alpha or beta particle, a number of excitations proportional to the energy of the particle, is produced.

2. The molecules of solvent come back to the ground state emitting a photon, exciting another solvent molecule or a fluorescent molecule.
3. The energy is finally transferred to the fluorescent substance which emits a photon with a certain wavelength. If this wavelength is not high enough to be detectable by the photomultiplier, it is necessary to use a second fluorescence substance.
4. The photomultiplier detects the flash of photons and transforms it to an electric pulse.

Every electric pulse corresponds to the detection of a flash of photons and the intensity of each pulse is proportional to the number of photons from the detected flash. The computer counts the number of flashes detected and classifies every flash of photons in an energy channel proportional to the number of photons detected from this flash. A spectrum is created from the count rate of flashes detected, the independent variable, and the energy channels where is classified each one, which represents the dependent variable. The position of the spectrum on the abscissas axis gives information about the energy of the flash of photons detected. Strong beta emitting radionuclides will produce displaced spectra towards high energy channels while low beta emitting radionuclides will be displaced towards low energy channels.

As it has been said, for every disintegration, a flash of photons is produced, and the number of photons detected from every flash is dependent on four factors:

- Energy of the beta (or alpha) particle emitted.
- Interferences during transmission energy stages.
- Capacity of the scintillator to generate photons.
- Capacity of the photomultiplier to detect photons.

These four factors are those that will allow or not that all disintegrations produced are detected, as flashes of photons, by the photomultiplier. In order to evaluate how a scintillator system is capable to detect the disintegrations emitted by a radioactive source, detection efficiency parameter is defined.

3.2.1. Detection efficiency and quenching

Detection efficiency is defined as the number of flashes of photons detected compared to the total number of disintegrations produced by the radioactive source. As it can be observed in the next equation, it is calculated like the percentage of count rate of flashes of photons detected by the photomultiplier, subtracting counts from the blank, compared to the activity of the radionuclide in the measurement vial, in disintegrations per unit of time.

$$\text{Detection efficiency} = \frac{\text{Sample counts} - \text{Blank counts}}{\text{Activity}} \times 100$$

Detection efficiency is related with the four factors commented in the previous section. High energy particles and more sensitive detectors will have higher detection efficiencies, while interferences during transmission energy stages will decrease the detection efficiency. These interferences are called quenching interferences and may have a high impact on detection efficiency parameter.

There are different types of quenching interference depending on the nature of the interference [1,2,4]:

- Particle quenching: The alpha or beta particle emitted by an active sample must travel some distance before interacting with a solvent molecule. If this particle interacts with another molecule or material before transferring its energy, this energy can be lost.
- Ionization quenching: In some cases, the solvent molecules become ionized instead of excited. If an excited state molecule is ionized, it will not come back to the ground state, and the energy will not pass to another molecule.
- Chemical quenching: During the processes of energy transmission between the molecules of solvent or polymer and fluorescent ones, other compounds of the sample can absorb this energy preventing photons to be produced.
- Colour quenching: If any substance present in the sample absorbs light at the same wavelength of the photons emitted, these photons will be absorbed and will not reach the detector.
- Optical quenching: On its way to the detector, photons pass through different mediums like air, aqueous solution, glass from the measuring vial or even polymer in plastic scintillation. These changes of medium imply refraction index changes which produce optical effects like reflection, refraction or absorption. These effects can decrease the number of photons detected by the photomultiplier.

There are several methods to calculate the impact produced by all these quenching interferences. In this case, the parameter used is the Spectral Quench Parameter (SQP(E)) calculated by the detector itself using an external gamma source. To calculate it, a reference spectrum is created from the external source, usually ^{152}Eu , and the energy channel of this spectrum which limits the 99,5% of the total counts corresponds to the SQP value [2].

Therefore, the SQP is related with the position of the spectrum: spectra displaced towards high energy channels will be related with high SQP values.

In general, a high detection efficiency will be related with low quenching levels which are represented by high SQP values (above 700).

3.2.2. Liquid scintillation

Liquid scintillation (LS) is the main and more used scintillation method of beta emitters determination. Sample preparation is very simple: the active sample is mixed in a vial with a scintillation cocktail which contains a liquid mixture of an aromatic solvent, such as toluene, and one or two scintillators substances, usually PPO and POPOP, (primary and secondary fluorophores). In case of aqueous sample measurement, surfactants are added to create an emulsion in order to keep a homogenous medium.

The distance between the radionuclide and the scintillator substance is very short in the emulsion, so quenching particle is negligible. The homogeneous medium avoids index refraction changes, so optical quenching is minimized, too.

Because of these, it often offers great detection efficiency results and low limits of detection are achieved. For strong beta emitting radionuclides, like ^{90}Sr , detection efficiency obtained is near 100% in many cases. For very weak beta emitting radionuclides, like ^3H , detection efficiencies up to 40% can be achieved.

However, a disadvantage of this technique is the production of mixed wastes which contain radioactive samples mixed with organic solvents. So, very contaminant and difficult to manage wastes are produced.

3.2.3. Plastic scintillation

Plastic scintillation method has the same mechanism as LS. The main difference is the use of a polymer as solid solvent. As a solid, the polymer can be prepared of any shape and size. In form of microspheres, it can be used as an alternative to liquid scintillation. The plastic scintillation microspheres (PSm) are, usually, prepared with polystyrene and contain the fluorescents molecules of PPO and POPOP, primary and secondary fluorophores, physically trapped inside them. Normally, prepared PSm are about 50 μm in order to minimize particle and optical quenching. Bigger microspheres increase particle quenching while smaller ones increase optical

quenching. In addition, a bigger size of PSm would make more difficult the determination of alpha particles which can only go through some microns in the sample medium to reach the scintillator.

In plastic scintillation, particle and optical quenching factors must be considered because of the heterogenous medium of the sample. The active radionuclide is not so close to the scintillator as in LS, so it is more difficult for the particle to reach the solvent and transfer its energy. For this reason, plastic scintillation often offers comparable detection efficiency results than LS for medium and high energy beta emitters, but lower for low energy beta emitters.

However, it presents some advantages over LS. First, the heterogenous medium avoids producing mixed wastes and allows reusing the polymer scintillator for other measurements. For the same reason, no liquid phases separation can be produced, which is a problem in LS of high salinity samples.

In addition, other substances can be added to the structure of the polymer to improve some qualities. For example, its stability can be increased for aggressive matrix sample measurements or a selective extractant can be added on the PSm surface to use it for the determination of a specific radionuclide from a complex sample. The set of a PSm with an extractant is called PSresin.

Since beta emitters are not monoenergetic, it is necessary to use a separation method in order to isolate the specific radionuclide from other interferences and then determine it. Solid phase extraction is used for this purpose and PSresin is a useful tool. PSresin allows extracting the specific radionuclide and measuring it in the detector directly because PSresin is formed by an extractant adsorbed to the scintillator itself (PSm). In Figure 1 [5], are represented the solid phase extraction and measurement stages using LS technique and PSresin, respectively.

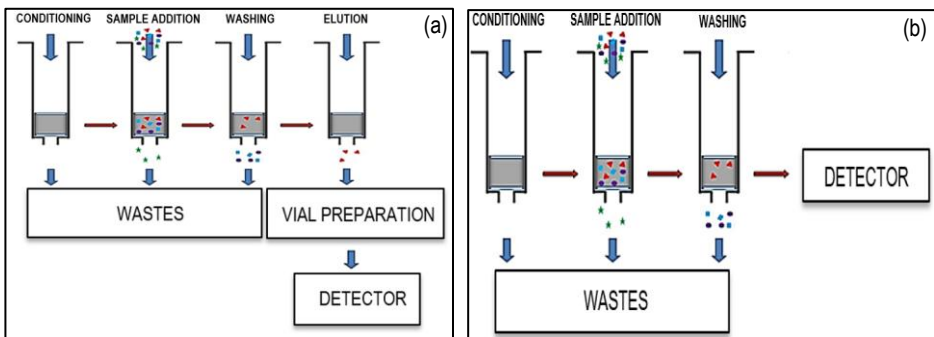


Figure 1. (a) Solid phase extraction and measurement stages with liquid scintillation.
(b) Solid phase extraction and measurement stages with PSresin.

Solid phase extraction and measurement using PSresin presents some advantages over LS:

- Less stages are needed for the solid phase extraction. The sample can be measured by the detector directly from the solid phase extraction cartridge, so elution stage is not needed and, therefore, procedural time is reduced.
- Less reactants are used: no elution stage and no vial preparing stage are needed.
- Less wastes are produced for the same reason.

However, the use of PSresin has two main problems. Preparation of PSresin include the immobilization of the extractant on the surface of the PSm. The most simply method is immobilization by impregnation [2, 5]. The main drawback of this process is that low breakthrough volumes are obtained and, therefore, the extractant is easily lost during the solid phase extraction. An alternative to the impregnation method is to get the extractant chemical linked through covalent bonds with the PSm rather than adsorbed. However, in this case, organic solvents are usually needed during the preparation process and this leads to the solubilization of PPO and POPOP's molecules which are lost.

On the way to solve these problems, the idea of these work is to use a polymerizable fluorescent solute for PSm preparation, so that PPO and POPOP are not needed and the polymer may act as scintillator itself. In addition, this polymer must have the possibility of getting chemical linked with an extractant.

Some previous studies [7] suggest the possibility of using carbazole derivates for plastic scintillation measurements. In the cited article, several experiments are done with derivates of carbazole with different roles within the scintillator system:

- Whole scintillator system. Using a polymer derivate or even forming a copolymer with styrene.
- Primary fluorophore. As PPO's substitute.
- Secondary fluorophore. As POPOP's substitute.

For PSresin development the aim is to use a carbazole derivate which can act as PPO and POPOP's substitute but, also, which could be polymerized easily for PSm preparation. It has been taken into account that the price must be affordable or easy to be synthesized in order to be a realistic and useful alternative. The chosen carbazole derivate was 9-vinylcarbazole (VK) which can be acquired from regular producers and may be polymerized to poly(9-vinylcarbazole) (PVK). Molecular structures of PPO, POPOP, VK and PVK are shown in Figure 2.

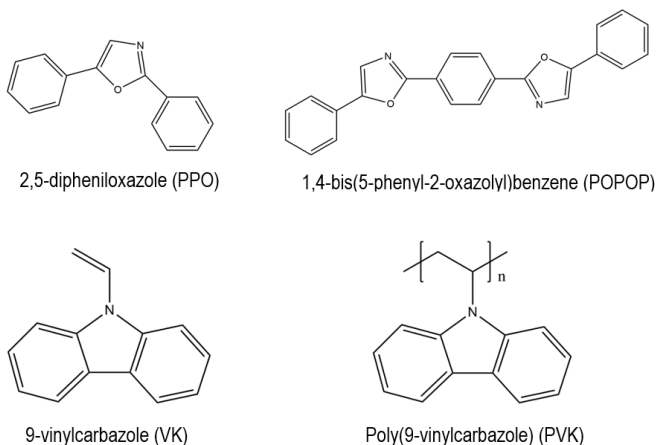


Figure 2. Molecular structures of PPO, POPOP, VK and PVK.

4. OBJECTIVES

The main objective of this study is the development of fluorescent polymeric microspheres based on 9-vinylcarbazole which can be used in plastic scintillation technique for radioactive emitters determination. To achieve this, two secondary objectives must be completed:

- To synthesize a fluorescent polymer based on poly(9-vinylcarbazole) from its monomer 9-vinylcarbazole.
- To evaluate the scintillation capacities of the fluorescent polymer based on poly(9-vinylcarbazole) by measuring standard solutions of beta and alpha emitting radionuclides.

5. EXPERIMENTAL SECTION

5.1. REAGENTS AND APPARATUS

All reagents used for the study classified by their respective supplier are:

- Reagents supplied by Sigma-Aldrich: Styrene ($\geq 99\%$), 9-vinylcarbazole (VK) (98%), poly(9-vinylcarbazole) (PVK), 2,5-dipheniloxazole (PPO) (99%) and 2,2'-Azobis(2-methylpropionitrile) (AIBN) ($\geq 98\%$).
- Reagents supplied by PanReac AppliChem: Dichloromethane (DMC) (99,8%) and Acetonitrile for HPLC.
- Reagent supplied by Carlo Erba Reagents: 1,4-bis(5-phenyl-2-oxazolyl)benzene (POPOP)
- Reagent supplied by Merck: Polyvinyl alcohol (PVA) ($\geq 98\%$).

Specific equipment has been used for the study. A 1220 Quantulus (Perkin Elmer) with multichannel analyzer (MCA) has been used for the scintillation measurements. A field emission scanning electron microscopy (FE-SEM) (Jeol-7100) from the scientific and technologic centers of the University of Barcelona (CCiT-UB) and an optical microscope SZ61 Stereo Microscope (Olympus) have been used to perform the images of the PSm synthesized. A Laser Diffraction Particle Size Analyzer LS 13 320 (Beckman Coulter) from the CCiT-UB has been used for granulometric analysis of PSm's size. A FT-IR Spectrometer Frontier (Perkin Elmer) from CCiT-UB with an accessory of attenuated total reflectance (ATR) has been used for IR characterization. A Cary Eclipse Fluorescence Spectrophotometer (Agilent Technologies) has been used for fluorescence spectroscopy measurements.

5.2. SYNTHESIS OF POLYMERS AND COPOLYMERS

In this section, it has been described the methodology of synthesis of polystyrene (PS) from styrene, poly(9-vinylcarbazole) (PVK) from 9-vinylcarbazol (VK) and two copolymers from mixtures of styrene and VK.

5.2.1. Synthesis of PS

First, styrene is purified by passing it through a syringe filled with glass wool and alumina and connected to the vacuum to accelerate the process. The purified styrene is poured into a 50 ml glass bottle using an automatic micropipette and an amount of initiator AIBN corresponding to 2%

of the total styrene's weight is added to the same bottle. The solution is homogenized by shaking it and it is purged by N₂ flow for 10 minutes. The bottle is immersed in paraffin oil at 75°C and agitation conditions for 24 hours.

5.2.2. Synthesis of PVK

The monomer of PVK, which is 9-vinylcarbazole (VK), is a solid, so there are two options for its polymerization. The first one is to melt the monomer, which melting point is 60-65°C, before polymerizing it and the second one is to dissolve it and polymerize the resultant solution.

- Monomer's melting (PVK-melt): The monomer, VK, is added to a glass bottle together with the 2% of initiator substance, AIBN. A complete homogenization is not achieved. The mix is purged carefully with N₂ flow for 10 minutes. The glass bottle is immersed in paraffin oil at 75°C under agitation for 24 hours.
- Monomer's dissolution (PVK-diss): The VK is dissolved in acetonitrile (7 g in 40 ml of acetonitrile) in a glass bottle. 2% of AIBN is added to the bottle. The solution is homogenized by shaking it and it is purged with N₂ flow for 10 minutes. The bottle is immersed in paraffin oil at 75°C under agitation for 24 hours. Product obtained must be left in an oven at 40°C for 48 hours in order to let evaporate all the acetonitrile.

5.2.3. Synthesis of copolymers of PS and PVK

Two different copolymers, from styrene and VK mixture, have been prepared. The first one, from 98% of styrene and 2% of VK and the second one, from 90% of styrene and 10% of VK. VK is soluble in styrene, so polymerization method used is the same as described in section 5.2.1. for polystyrene's synthesis. Two copolymers of PS/PVK (98:2 and 90:10) have been obtained.

5.3. PREPARATION OF PSm: EXTRACTION/EVAPORATION METHOD

PSm for scintillation measurements have been prepared using the polymers synthesized as it has been explained in the previous section.

The method used for PSm preparation is called microencapsulation by solvent extraction/evaporation [8]. This method consists in mixing, under agitation conditions, 1.2 L of an aqueous solution (Milli-Q water) of PVA 1%, saturated with 24 ml of dichloromethane (DCM), with 150 ml of an organic phase of DCM containing, dissolved, a total of 15 g of polymer and fluorescent substances (if used). The organic phase is added, slowly, into the aqueous solution

using a dropping funnel as it is shown in Figure 3. Because of the agitation and the presence of a surfactant (PVA), small drops of the organic phase remain suspended in the aqueous phase. DCM is slowly extracted by water and at the same time it is evaporated. As droplets lose the DCM progressively, they are transformed, little by little, into microspheres of the polymer used. The mixture is left 24 hours at 450 rpm and 25°C to be sure that all DCM has been evaporated. After this, the obtained PSm are filtered with a Büchner funnel and washed several times with Milli-Q water and ethanol. Finally, they are placed in an oven for 24 hours at 40°C.



Figure 3. Example of three simultaneous organic phase addition stages during extraction/evaporation procedure.

All PSm have been prepared following this methodology only changing organic phase composition. In Table 1, composition and nomenclature used for every PSm prepared are shown.

Name	PS	PVK	Others
PSm.ref	97.95%	-	2% PPO + 0.05% POPOP
PSm.PSt	100%	-	-
PSm.PVK-melt	-	100% PVK-melt	-
PSm.PVK-diss	-	100% PVK-diss	-
PSm.mix2-melt	98%	2% PVK-melt	-
PSm.mix10-melt	90%	10% PVK-melt	-
PSm.mix2-diss	98%	2% PVK-diss	-
PSm.mix10-diss	90%	10% PVK-diss	-
PSm.mix2-comm	98%	2% commercial PVK	In 300 ml of DCM
PSm.mix10-comm	90%	10% commercial PVK	In 300 ml of DCM
PSm.cop2	PSm prepared using copolymer prepared from 98% of styrene and 2% of VK		
PSm.cop10	PSm prepared using copolymer prepared from 90% of styrene and 10% of VK		

Table 1. Name of every kind of PSm prepared and its respective composition.

PSm of PS/PVK mixture using commercial PVK have been prepared using 300 ml of DCM instead of 150 ml due to a difficult dissolution of this PVK in DCM. Only PSm.mix10-comm have been obtained in form of microspheres. The only procedural difference between 2% and 10% mixtures is that organic phase of PS/PVK 10% has been filtered before extraction/evaporation procedure in order to remove some rests of polymer which couldn't be dissolved. The blocks of mixture of PS/PVK 2% obtained have been grinded with a mortar and used for scintillation measurements in order to get SQP(E) values information.

5.4. MEASUREMENT VIALS PREPARATION

In order to test the scintillation capability of the PSm obtained, measurement vials are prepared. Scintillation measurements are done with diluted solutions prepared from the standards. A ^{14}C active stock solution of $136 \pm 2 \text{ Bq g}^{-1}$ in an aqueous solution containing $50 \mu\text{g g}^{-1}$ of glucose and 1 mg g^{-1} of formaldehyde is prepared from a standard of $44.6 \pm 0.5 \text{ kBq g}^{-1}$ in the same medium from CERCA-LEA (Pierrelatte, France).

A $^{90}\text{Sr}/^{90}\text{Y}$ active stock solution of $26.0 \pm 0.1 \text{ Bq g}^{-1}$ containing Sr^{2+} ($100 \mu\text{g g}^{-1}$) and Y^{3+} ($100 \mu\text{g g}^{-1}$) in 0.1 M HCl is prepared from a standard of $4.07 \pm 0.02 \text{ kBq g}^{-1}$ in the same medium supplied by Amersham International (Buckinghamshire, England)

A ^{241}Am solution (Am^{3+}) of 43.1 Bq g^{-1} containing $100 \mu\text{g ml}^{-1}$ of EuCl_3 in 1 M HCl prepared from an active solution of 200 kBq g^{-1} in the same medium supplied by Eckert & Ziegler (Berlin, Germany)

Every vial is prepared with 1.5 g of the tested PSm and 0.625 ml of diluted solutions prepared from the active stock solutions of ^{14}C , $^{90}\text{Sr}/^{90}\text{Y}$ and ^{241}Am . For every series of measures, a blank is done with 1.5 g of the tested PSm and 0.625 ml of Milli-Q water. Before measuring, every vial is shaken using a vortex mixer for 3 minutes to homogenize the radioactive solution with the scintillator (PSm). The approximate final activity in every measurement vial is about 6.5 Bq for ^{14}C determinations, 1.5 Bq for $^{90}\text{Sr}/^{90}\text{Y}$ and 3 Bq for ^{241}Am . The exact activities are determined by active solution's weight in every vial.

Vials are introduced in 1220 Quantulus to count the flashes of photons per minute (cpm) from every vial for one hour and to calculate the SQP value. Counts are classified in 4096 energy channels but only the first 1024 correspond to emissions produced by the sample. From this information, detection efficiency spectra and count rate spectra are built.

5.5. DATA TREATMENT

Current activities of the standards have been calculated using the references activities shown in Table 2 and the nuclear decay activity equation:

$$A = A_0 * e^{-\ln(2) * \frac{\Delta t}{t_{1/2}}}$$

Radionuclide	Reference Activity(Bq/g)	Reference date	Calculated activity(Bq/g)	Current date
¹⁴ C	136.0	05/12/2001	135.7	15/10/2018
⁹⁰ Sr/ ⁹⁰ Y	38.5	01/06/2002	26.0	15/10/2018
²⁴¹ Am	43.2	13/12/2016	43.1	15/10/2018

Table 2. Reference activities and current activities of the standard solutions used for the study.

Count rate spectrum from every measurement is smoothed using a Savitzky-Golay algorithm from MATLAB to improve its visualization.

A net spectrum is obtained by subtracting blank solution count rate from the active count rate spectra. The ratio, in percentage, between the net spectrum and the respective activity of each vial, corresponds to the detection efficiency spectrum. Detection efficiency of every measurement is calculated as the integration of energy channels from the detection efficiency spectrum in the selected range.

The quenching parameter SQP(E) is calculated automatically by the detector using an external gamma ray source.

6. RESULTS AND DISCUSSION

The results and discussion section of this study is divided in two main parts. The first one, involve all the procedures and results related with the synthesis of PVK through VK's polymerization. Two different methods of synthesis have been followed and several differences have been observed between them.

The second main part consists in evaluating the scintillation measurements results of different PSm prepared from the polymers and copolymers previously synthesized with different proportions of PS and PVK.

6.1. SYNTHESIS OF PVK AND PS

Two different methods of polymerization of VK to synthesize PVK have been used. The first one consisting in heating the VK, mixed with 2% of AIBN, until it melts at 60-65°C and then polymerize it by heating at 75°C for 24h. The second one consisting in dissolving VK in acetonitrile (7 g in 40 ml) and later polymerize the resultant solution in the same way.

Apart from this, polystyrene has been synthesized from styrene in order to make scintillation results more comparable. Since styrene is in liquid state no stage of melting or dissolving is needed before to its polymerization.

6.1.1. Synthesis of PVK

6.1.1.1. PVK-melt

The product obtained by VK's melting and polymerization is a yellow porous block. In Appendix 1 a descriptive image of its look can be found. It has several orange zones which could be areas of higher density of polymer due to a higher initial amount of AIBN. This heterogeneity might be the result of a difficult homogenic mix between VK and the initiator, AIBN.

The monomer and the product obtained look similar, therefore, several solubility experiments have done in order to check that the product obtained is not the monomer. In Table 3, solubility tests results using ethanol, methanol and dichloromethane are shown.

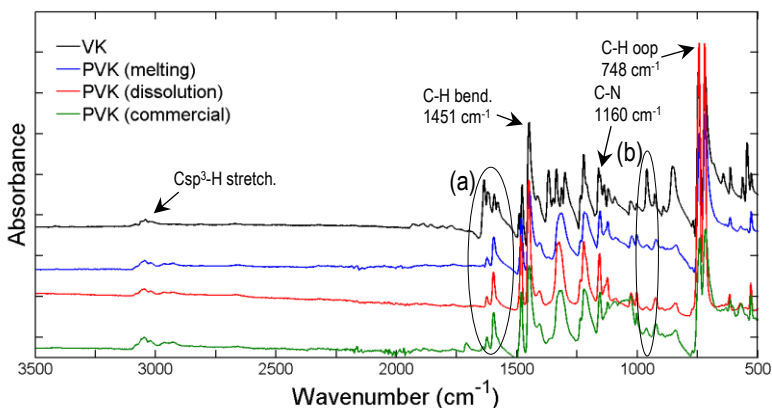
Solvent	Monomer (VK)	Product obtained
Ethanol	Soluble	Insoluble
Methanol	Soluble	Insoluble
Dichloromethane	Soluble	Soluble

(a) 0.1 mg in 0.5 ml approx.

Table 3. Solubility tests to the monomer and product obtained.

Solubility tests prove that the product obtained is not the monomer for their different behavior in front of ethanol and methanol.

In addition, IR spectra of monomer, product obtained from monomer's melting and commercial PVK (Figure 4) have been compared in order to confirm that the product obtained is PVK. More characteristic common bands in VK and PVK structures have been identified [6,7].



(a) Characteristic C=C stretching band at 1638 cm^{-1} from a terminal vinyl, only observed in VK's spectrum. Aromatic C=C bands are present in all three spectra ca. 1600 cm^{-1} .

(b) Characteristic vinyl's group bending band at 958 cm^{-1} , only observed in VK's spectrum.

Figure 4. Normalized absorbance IR spectra of VK, PVK-melt, PVK-diss and commercial PVK.

Characteristic bands of vinyl group, only present in monomer's structure, are only observed in VK's IR spectrum. In addition, IR spectra of PVK polymerized and commercial PVK present the same bands. Therefore, it is concluded that the product obtained is PVK.

6.1.1.2. PVK-diss

Product obtained by polymerizing the solution of VK dissolved in acetonitrile is totally white and homogenous. A descriptive image of it can be found in Appendix 1. It seems like all impurities have rest at the bottom of the glass bottles what allows to discard them easily. This procedure of synthesis requires two more stages than monomer's melting method. First, product must be dissolved in acetonitrile and, second, all acetonitrile must be removed from final product by evaporation in an oven for 48 hours.

Same solubility tests as PVK-melt are done to the product obtained by VK's dissolution and the same results have been obtained. Therefore, it is also concluded that the product obtained is no longer the monomer.

As well as for PVK-melt, IR spectra of monomer, product obtained by monomer's dissolution and commercial PVK have been compared in Figure 4. IR spectra also confirm that the product obtained is PVK.

6.1.2. Synthesis of PS

Polystyrene has been synthesized from purified styrene's polymerization using a 2% of AIBN. The product obtained is colorless and very hard. It has been dissolved in DCM to be able to get it out from the glass bottle. In Appendix 1, a descriptive image of its appearance can be found.

The correct polymerization of the styrene is easily observable by the change of state from liquid to solid.

6.2. SCINTILLATION CAPABILITY OF PSm OF PS AND PVK

Size and morphology of every kind of PSm prepared have been studied through a granulometric analysis and images performed with SEM and optical microscope. Also, the evaluation of the scintillation capability of all PSm has been done by measuring count rates of series of vials including a blank and standards of a medium beta emitter (^{14}C), a strong beta emitter ($^{90}\text{Sr}/^{90}\text{Y}$) and an alpha emitter (^{241}Am). Each vial contains 1.5 g of the tested PSm and 0.625 ml of the diluted standard active solution (except the blank vial which contains the same amount of Milli-Q water).

6.2.1. PSm of PS

6.2.1.1. PSm.ref

PSm of PS with PPO and POPOP will be used as reference PSm (PSm.ref).

The granulometric analysis has concluded that the median size of all PSm is 49 μm . The particle size distribution is represented in a graphic which can be found in Appendix 2. In Figure 5, two images performed with SEM and optical microscope are shown. These images confirm that PSm prepared are of about 50 μm , spherical, transparent and quite homogenous.

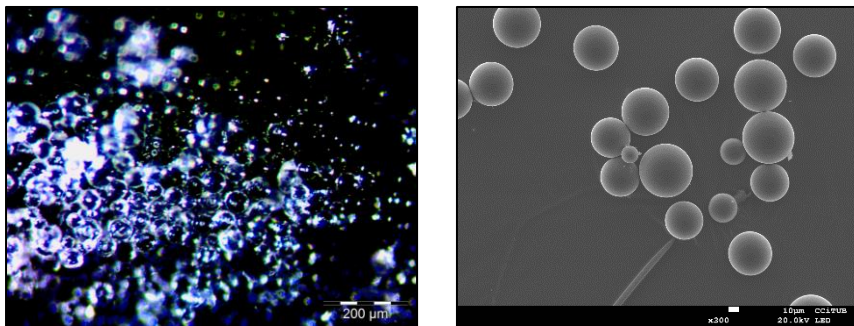


Figure 5. Images of PSm of PS with PPO and POPOP performed with optical microscope (left) and with SEM (right).

Count rate spectrum obtained can be observed in Figure 6. Count rate of the blank is 0.96 cpm, a common value for this kind of scintillators. As it has been explained in introduction section, the position of the spectrum is directly related with the levels of quenching of the measurement. For a same radionuclide, if the spectrum is displaced towards higher energy channels, usually, higher SQP(E) values are obtained and, therefore, higher detection efficiency.

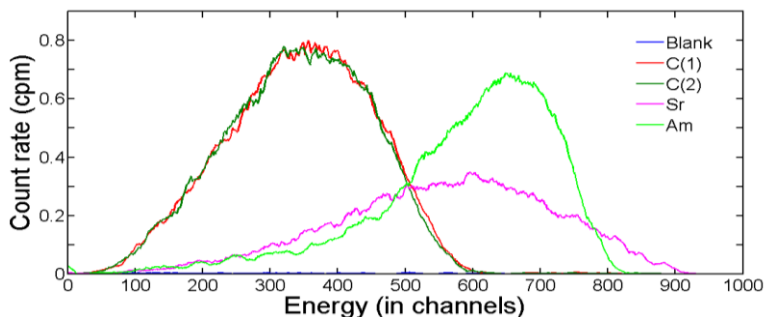


Figure 6. Count rate spectrum of scintillation measurements with PSm.ref

In Table 4, SQP(E) and detection efficiency values are shown. SQP(E) values are around 800 what means that quenching interferences are low and, therefore, high detection efficiency values have been achieved. For ^{14}C , a detection efficiency of 59.0(0.4)% has been obtained because ^{14}C is a medium-energy beta emitter and not all beta particles are detected.

Detection efficiency of $^{90}\text{Sr}/^{90}\text{Y}$, both strong beta emitters, is higher than 100% because after ^{90}Sr beta decay, it is transformed to ^{90}Y which is also a beta emitter. Therefore, detection efficiency obtained from ^{90}Sr is half of the total which represents the sum of both beta emissions. In this case, the detection efficiency for ^{90}Sr is 92.3% which means that almost all beta particles emitted are detected.

For ^{241}Am , an alpha emitter, a 96.4 % of detection efficiency has been obtained. For PSm of about 50 μm , almost all alpha particles have been detected.

Sample	Detection efficiency (%)	SQP (E)
Blank	-	813.7
^{14}C (1)	59.3	812.1
^{14}C (2)	58.7	806.8
$^{90}\text{Sr}/^{90}\text{Y}$	184.6	804.1
^{241}Am	96.4	797.3

Table 4. Scintillation measurements results of PSm.ref.

Results obtained for ^{14}C , $^{90}\text{Sr}/^{90}\text{Y}$ and ^{241}Am determinations are similar to others obtained in previous studies [3] with a similar PSm size, therefore, they can be considered valid results and they will be taken as reference results for this study.

6.2.1.2. PSm.PSt

As a control group, PSm of PS without fluorescent molecules (PPO and POPOP) have been prepared (PSm.PSt).

Count rate obtained from the blank is 0.72 cpm. As it can be observed in Figure 7, all spectra represented are displaced toward lower energy channels than they were in PSm.ref. The highest energy channel for ^{90}Sr and ^{241}Am is almost 600, while for ^{14}C measurements is about 300. All spectra are displaced about 300 channels to lower energies compared to spectra from PSm.ref. This means that not all energy is transformed into detectable photons.

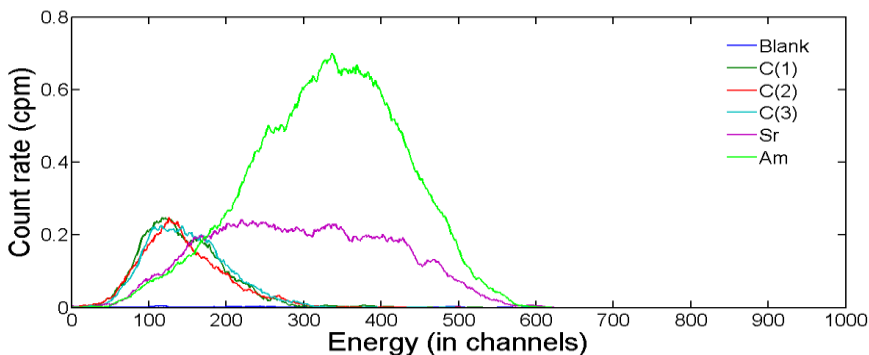


Figure 7. Count rate spectrum of scintillation measurements with PSm of only PS.

Therefore, lower SQP(E) and detection efficiency values are obtained as it can be checked in Table 5. For ^{14}C , only 7.3(0.4)% of detection efficiency is achieved.

Sample	Detection efficiency (%)	SQP (E)
Blank	-	484.4
^{14}C (1)	7.6	482.7
^{14}C (2)	6.8	500.7
^{14}C (3)	7.5	487.6
$^{90}\text{Sr}/^{90}\text{Y}$	107.9	487.0
^{241}Am	72.9	492.7

Table 5. Scintillation measurements results of PSm.PSt.

The scintillation results of PSm.PSt will be used, also, as reference.

6.2.2. PSm of PVK

6.2.2.1. PSm.PVK-melt

Scintillation measurements have been done using PSm of PVK polymerized by VK's melting (PSm.PVK-melt).

Size and morphology of PSm prepared have been studied in the same way as PSm.ref in order to compare each other. The granulometric analysis has concluded that the median size of all PSm of PVK is 44 μm . The particle size distribution is represented in a graphic which can be found in Appendix 2. Images obtained with SEM and optical microscope (Figure 8) confirm that PSm of PVK have a very similar size and morphology to PSm.ref. The only difference detected is

a higher number of craters, due to collisions between microspheres, on PSm of PVK's surface (Figure 8-d) probably because PVK is softer than PS.

For all this, it is concluded that PSm.PVK-melt can be prepared of the same size and shape than PSm.ref through a same method of PSm preparation.

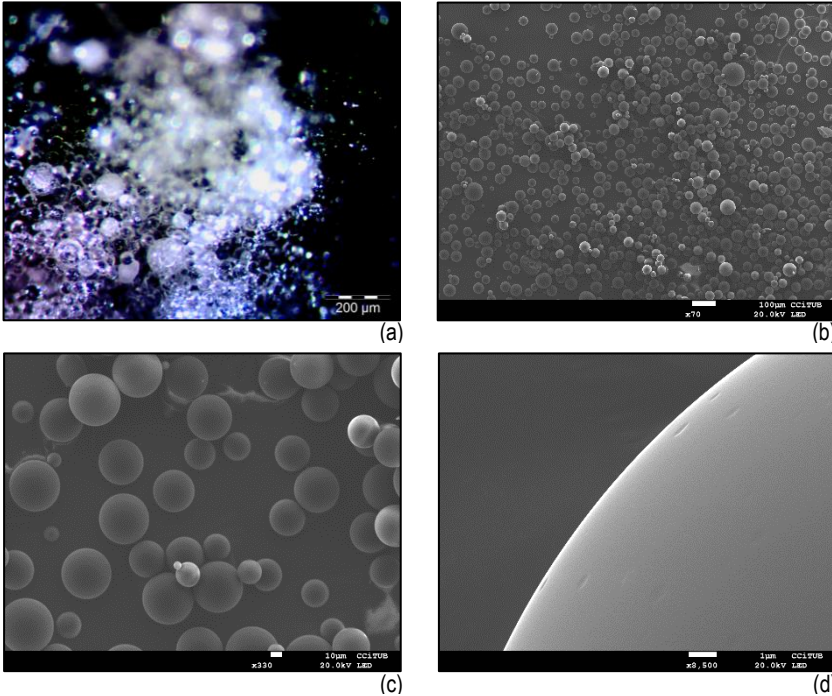


Figure 8. Images of PSm of PVK obtained by VK's melting performed with an optical microscope (a) and with SEM (b-d).

Count rate spectra obtained in scintillation measurements are shown in Figure 9. A very high intensity peak in the first 200 channels range is observed. This peak corresponds to very low energy emissions which do not represent sample's count rate because even the blank shows this peak. Count rate from the blank has been 85.52 cpm. The most plausible hypothesis is that this peak is caused by luminescence phenomenon which could mean that these photons detected are emitted by PVK itself for some possible reasons:

- Photoluminescence: photon emission by previous absorption of photons from ambient light.
- Chemiluminescence: emission of light as a result of a chemical reaction.

- Bioluminescence: emission from a biochemical reaction involving a living organism.
- Thermoluminescence: emission of previous absorbed energy when a substance is heated.

Mainly, two of these types of luminescence can interfere in the scintillation measurements, which are photoluminescence and chemiluminescence [4]. In order to find out which one is the responsible of the luminescence phenomenon detected, several tests have been done. It has been tested if changes in scintillation results were observed when sample was exposed to light and, immediately after, measured. The results of these tests concluded that the phenomenon was not photoluminescence because count rate of the blank did not increase when exposed to light. In addition, results show that the phenomenon decreases with time what agrees with a chemical reaction that is being completed.

Therefore, the main hypothesis is that the phenomenon corresponds to chemiluminescence which could be produced for the unfinished polymerization reaction of the monomer. Luminescence phenomenon is a problem because detection efficiency can not be calculated using the total count rate. The first 200 energy channels are not used in order to discard luminescence count rate.

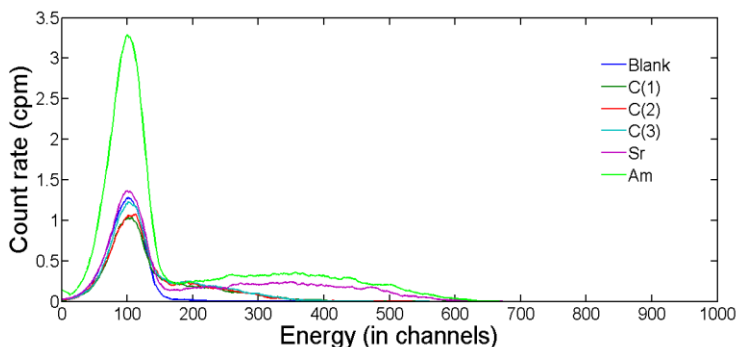


Figure 9. Count rate spectrum of scintillation measurements with PSm.PVK-melt.

On the other hand, it can be observed that the spectra are displaced towards low energy channels what agrees with low SQP(E) values shown in Table 6. High quenching levels are present and, as a result of this, very low detection efficiency values are achieved. For ^{14}C , a detection efficiency of 4.6(0.2)% has been obtained.

Sample	Detection efficiency (%)	SQP (E)
Blank	-	544.5
^{14}C (1)	4.4	544.8
^{14}C (2)	4.5	537.3
^{14}C (3)	5.0	547.7
$^{90}\text{Sr}/^{90}\text{Y}$	88.4	547.0
^{241}Am	52.0	541.4

Table 6. Scintillation measurements results of PSm.PVK-melt.

It has been discarded the use of PSm.PVK-melt for scintillation measurements due to a very low detection efficiency results, high levels of quenching and a high luminescence phenomenon.

6.2.2.2. PSm.PVK-diss

As it has been found that PSm.PVK-melt can not be used for scintillation measurements, they have been also performed using PSm of PVK obtained by polymerization of VK dissolved in acetonitrile (PSm.PVK-diss).

In Figure 10, can be observed, again, a high intensity peak in the first 200 energy channels range corresponding to luminescence phenomenon. In this case, count rate of the blank is 29.36 cpm. The peak is less intense than the one obtained with PSm of PVK by VK's melting what agrees with less count rate of the blank. Therefore, it can be concluded that the luminescence phenomenon observed is directly related with the polymerization method used for the synthesis of PVK. This fact, supports the hypothesis that the luminescence phenomenon is produced by

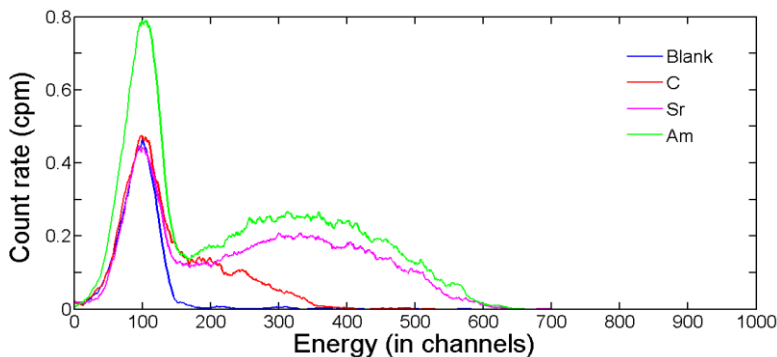


Figure 10. Count rate spectrum of scintillation measurements with PSm.PVK-diss.

chemiluminescence from the polymerization reaction. Maybe, a better homogenization of VK with the initiator (AIBN) and, therefore, a better heat transfer during the synthesis of PVK by VK's dissolution, could be the responsible of a more completed polymerization reaction. However, luminescence of the blank is not negligible and, again, the first 200 energy channels have been discarded for detection efficiency calculation.

In Table 7, detection efficiency and SQP(E) values are shown. As it is observed, the results are not significantly different from those obtained using PSm.PVK-melt. Therefore, it is concluded that the method of polymerization of VK's does not affect the results of scintillation measurements obtained.

Sample	Detection efficiency (%)	SQP (E)
Blank	-	524.4
¹⁴C	4.2	528.9
⁹⁰Sr/⁹⁰Y	82.0	533.6
²⁴¹Am	41.1	534.1

Table 7. Scintillation measurements results of PSm.PVK-diss.

Moreover, it has been observed that PSm.PVK-diss have similar levels of quenching as PSm.PVK-melt and both have detection efficiency values much lower than results of PSm.ref. Both PSm of PVK have similar morphology and size to PSm.ref. Therefore, it can be concluded that particle, optical and ionizing quenching are equal in both cases. For this reason, it is thought that high levels of quenching in PSm of PVK measurements could come from color quenching, because PSm of PVK are yellow, or chemical quenching, because maybe the energy transmission between molecules is not good enough and some of this energy is lost.

In addition, the luminescence phenomenon produced by PVK is an added disadvantage. For these reasons, it has been discarded the use of both PSm of PVK for scintillation measurements.

6.3. SCINTILLATION CAPABILITY OF PSm OF PS/PVK MIXTURE

As it has been proved that PVK can not act as whole scintillator system for scintillation measurements, next experiments will consist in using PS as solvent and PVK as a substitute of PPO and POPOP. Therefore, PSm from mixtures of PS and PVK have been prepared using PVK-melt, PVK-diss and commercial PVK. Proportions chosen for each PSm's preparation have been:

- 2% of PVK and 98% of PS (same proportion as PPO in PSm.ref)
- 10% of PVK and 90% of PS

In order to check if PVK can act as PPO and POPOP's substitute in scintillation measurements, fluorescent emission spectra of PPO, POPOP and PVK have been measured. If PVK can be used as substitute of PPO or POPOP it must have a similar emission wavelength than PPO or POPOP.

As it can be seen in Figure 11, PVK has very similar emission wavelengths as PPO. They both emit at 375 nm. The peaks observed at 300 nm and 350 nm match with the excitation wavelengths of each one and are caused by a phenomenon called Rayleigh scattering. Therefore, PVK and PPO emit and get excited at same wavelength. Because of this, PVK should be able to be used as PPO's substitute. However, POPOP's gets excited at 350 nm and emits at 425 nm. Therefore, PVK should not be a good POPOP's substitute.

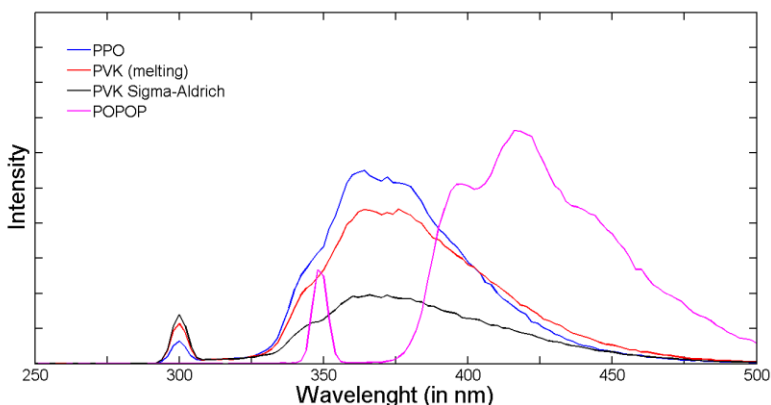


Figure 11. Emission spectra of PPO, POPOP, PVK-melt and commercial PVK.

6.3.1. PSm.mix-melt

PSm of PS/PVK mixtures of 2% and 10% have been prepared using PVK polymerized from VK's melting (PSm.mix2-melt and PSm.mix10-melt). Size and morphology of PSm prepared have been studied. The granulometric analysis has concluded that the median size of both PSm of PS/PVK is 47 μm . The particle size distribution of each one is represented in a graphic which can be found in Appendix 2. The images performed with SEM have confirmed that both PSm are of about 50 μm .

Scintillation measurements have been done using PSm.mix2-melt and PSm.mix10-melt. As it is observed in Figure 12, luminescence phenomenon has totally disappeared using PSm.mix2-melt and for PSm.mix10-melt very low, so it can be ignored. Count rate of the blank for PSm.mix2-melt is 0.79 cpm while for PSm.mix10-melt is 2.41 cpm.

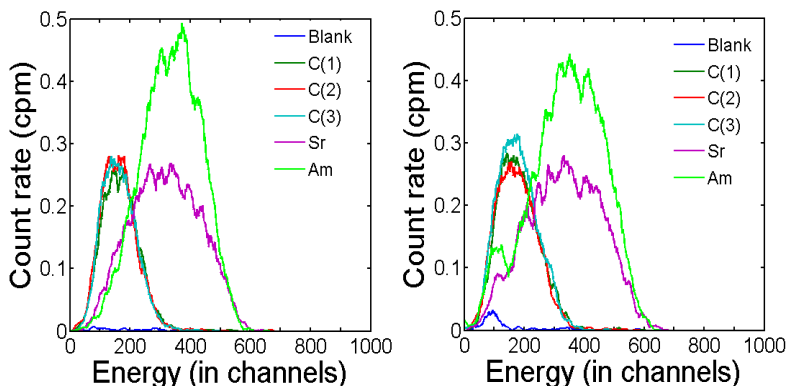


Figure 12. Count rate spectra of scintillation measurements with PSm.mix2-melt (left) and PSm.mix10-melt (right).

As it is shown in Table 8, detection efficiency values are, in general, higher than they were using PSm only of PVK. For ^{14}C , 10.4(0.3)% and 12.4(0.9)% have been obtained for PSm.mix2-melt and PSm.mix10-melt, respectively. However, these values are far from values of PSm.ref. One of the reasons might be that quenching interferences are still significant as it is represented with low SQP(E) values which are similar to those obtained before with PSm of PVK.

Both PSm prepared with mixtures of PS and PVK have similar results but, generally, the proportion with 10% of PVK has higher detection efficiency and SQP(E) values.

Sample	PSm.mix2-melt		PSm.mix10-melt	
	Detection efficiency (%)	SQP (E)	Detection efficiency (%)	SQP (E)
Blank	-	519.2	-	544.1
^{14}C (1)	10.1	520.6	11.9	537.9
^{14}C (2)	10.7	515.4	11.9	551.6
^{14}C (3)	10.5	503.0	13.4	526.6
$^{90}\text{Sr}/^{90}\text{Y}$	114.9	504.7	120.7	551.2
^{241}Am	63.9	514.9	70.1	545.6

Table 8. Scintillation measurements results of PSm.mix-melt.

6.3.2. PSm.mix-diss

Scintillation measurements have been done with PSm of PS/PVK 2% and 10% mixtures using PVK obtained by VK's dissolution in acetonitrile (PSm.mix2-diss and PSm.mix10-diss). As it can be observed in Figure 13, no luminescence phenomenon has been detected in any of both cases. Count rate of the blank for PSm.mix2-diss is 0.62 cpm while for PSm.mix10-diss is 0.77 cpm.

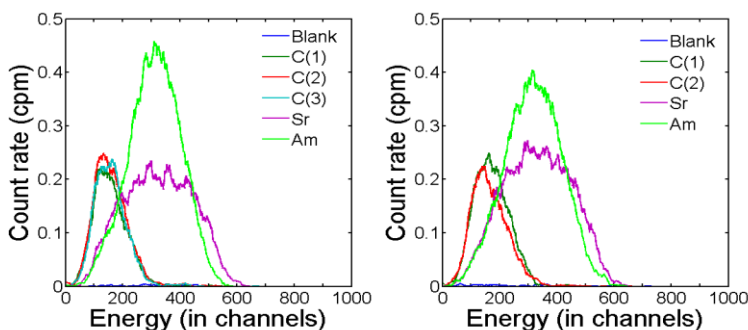


Figure 13. Count rate spectra of scintillation measurements with PSm.mix2-diss (left) and PSm.mix10-diss (right).

As it is shown in Table 9, detection efficiency and SQP(E) values are similar but, in general, lower, than those obtained with PSm.mix-melt. For ^{14}C , 8.3(0.5)% and 9.0(0.9)% have been obtained for PSm.mix2-diss and PSm.mix10-diss, respectively. As well as for PSm.mix-melt, the proportion of PS/PVK 10% has slightly better results than the ratio PS/PVK 2%. However, quenching interferences are still too high and, therefore, detection efficiency values are far from reference results obtained with PSm.ref.

Sample	PSm.mix2-diss		PSm.mix10-diss	
	Detection efficiency (%)	SQP (E)	Detection efficiency (%)	SQP (E)
Blank	-	506.7	-	536.6
^{14}C (1)	7.8	501.2	9.7	535.2
^{14}C (2)	8.8	496.5	8.3	532.7
^{14}C (3)	8.2	498.8	-	-
$^{90}\text{Sr}/^{90}\text{Y}$	103.3	516.5	120.1	535.0
^{241}Am	54.1	497.8	52.6	529.0

Table 9. Scintillation measurements results of PSm.mix-diss.

6.3.3. PSm.mix-comm

PSm of PS/PVK mixtures 2% and 10% have been prepared using commercial PVK (PSm.mix2-comm and PSm.mix10-comm). As it has been explained in experimental procedure section, commercial PVK has been difficult to dissolve in DCM. In the case of PS/PVK mixture of 2%, it was apparently dissolved but in the case of PS/PVK mixture of 10%, some polymer could not be dissolved. For this reason, the organic phase of PS/PVK 10% was filtered before extraction/evaporation procedure. However, during the synthesis, it was observed that PS/PVK mixture of 2% was not capable to produce microparticles. Images performed with SEM (Figure 14) confirm that only mixture of PS/PVK 10% has been obtained as PSm. Therefore, detection efficiency results of PS/PVK 2% are not very significant.

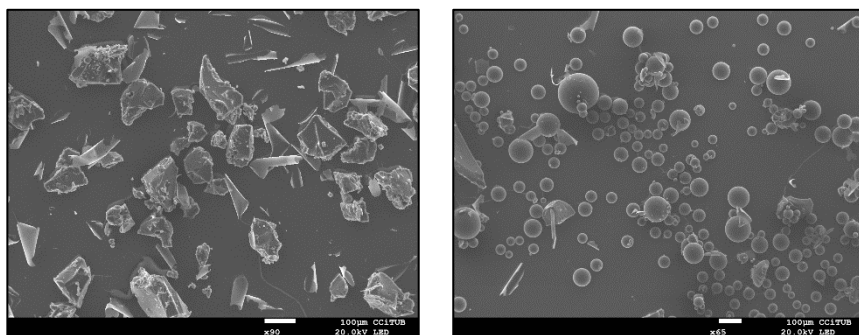


Figure 14. Images of “PSm.mix2-comm” (left) and PSm.mix10-comm (right).

This different behavior of commercial PVK in front of DCM and PVK polymerized from VK in this study, could be caused by the difference of chain length between PVK already prepared and the ones synthesized from VK. Commercial PVK has an average molecular weight of about $1,000,000 \text{ g mol}^{-1}$ which means that its chains are probably much longer than the ones of PVK synthesized from VK in this study. This could be the reason of the difference of solubility in DCM.

Count rate spectra obtained can be seen in Figure 15. No luminescence phenomenon has been detected in any of both cases because count rate for the blank is 0.54 cpm for PSm.mix2-comm and 0.45 cpm for PSm.mix10-comm. The spectra have similar positions than previous PSm of PS/PVK mixtures prepared and, therefore, lower than spectra of PSm.ref.

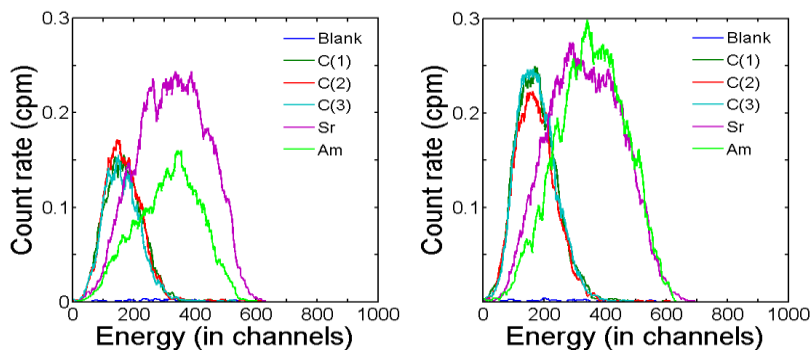


Figure 15. Count rate spectra of scintillation measurements with PSm.mix2-comm (left) and PSm.mix10-comm (right).

Detection efficiency and SQP(E) values, shown in Table 10, are very similar to those obtained with PSm.mix-melt and PSm.mix-diss. For ^{14}C , a detection efficiency of 5.9(0.4)% and 9(1)% is achieved for PSm.mix2-comm and PSm.mix10-comm, respectively. Detection efficiency of PSm.mix2-comm is significantly lower than PSm.mix2-melt and PSm.mix2-diss probably because it could not be prepared as microspheres.

Sample	PSm.mix2-comm		PSm.mix10-comm	
	Detection efficiency (%)	SQP (E)	Detection efficiency (%)	SQP (E)
Blank	-	497.7	-	520.1
^{14}C (1)	6.0	498.0	8.4	517.6
^{14}C (2)	6.3	488.5	9.3	522.6
^{14}C (3)	5.5	491.6	10.5	526.1
$^{90}\text{Sr}/^{90}\text{Y}$	104.8	510.9	122.0	529.9
^{241}Am	20.1	495.7	43.2	538.6

Table 10. Scintillation measurements results of PSm.mix-comm.

In summary, the use of commercial PVK offers similar results as both PVK synthesized from VK, but it is not appropriate for microspheres preparation following the standard methodology because of its difficult dissolution in DCM.

6.4. SCINTILLATION CAPABILITY OF PSm OF COPOLYMER PS/PVK

As it has been proved that the main quenching interference is not color quenching because all PSm of mixture PS/PVK obtained are white, another hypothesis is raised. Maybe high levels of quenching come from a difficult energy transfer stage between the chains of PS and PVK in PSm prepared from their mixture. Therefore, it has been analyzed the scintillation capability of PSm prepared with a copolymer of PS and PVK in same proportions as previous mixtures used: 2% PVK / 98% PS (PSm.cop2) and 10% PVK / 90% PS (PSm.cop10).

No luminescence phenomenon has been detected in neither of the two cases as it can be observed in both count rate spectra from Figure 16. Count rate of the blank is 1.09 cpm for PSm.cop2 and 1.13 cpm for PSm.cop10. In addition, count rate spectra are significantly more shifted towards high energy channels than they were those obtained with PSm of PVK and with any PSm of mixture PS/PVK.

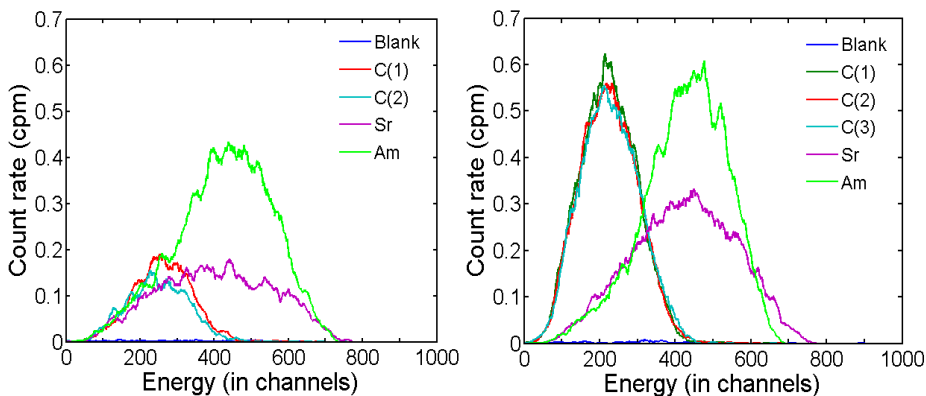


Figure 16. Count rate spectra of scintillation measurements with PSm.cop2 (left) and PSm.cop10 (right).

Shift positions of the count rate spectra are reflected in the obtained results, shown in Table 11, as higher SQP(E) values. It can be concluded that levels of quenching are lower due to a better energy transmission between chains of PS and PVK when they are linked as a copolymer. However, this improvement is partially reflected in detection efficiency values. Only PSm.cop10 have obtained significant higher detection efficiency results, while PSm.cop2 have obtained similar values to previous PSm studied. For ^{14}C , 8(1)% and 29.6(0.5)% have been obtained for PSm.cop2 and PSm.cop10, respectively.

Sample	PSm.cop2		PSm.cop10	
	Detection efficiency (%)	SQP (E)	Detection efficiency (%)	SQP (E)
Blank	-	643.7	-	630.1
¹⁴ C (1)	9.1	659.0	30.1	625.7
¹⁴ C (2)	7.4	649.1	29.2	631.1
¹⁴ C (3)	-	-	29.6	638.9
⁹⁰ Sr/ ⁹⁰ Y	92.6	651.1	155.8	631.0
²⁴¹ Am	72.7	633.9	83.5	630.3

Table 11. Scintillation measurements results of PSm of copolymers of PS/PVK.

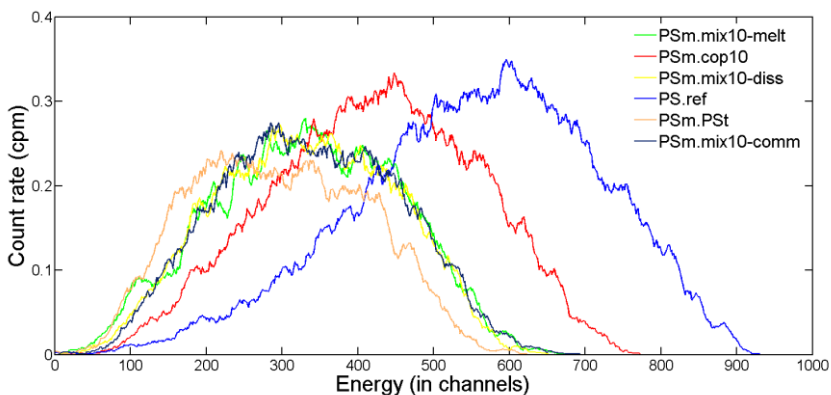
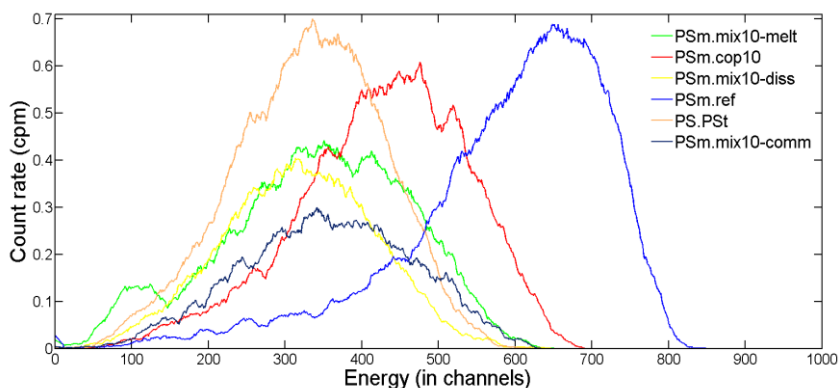
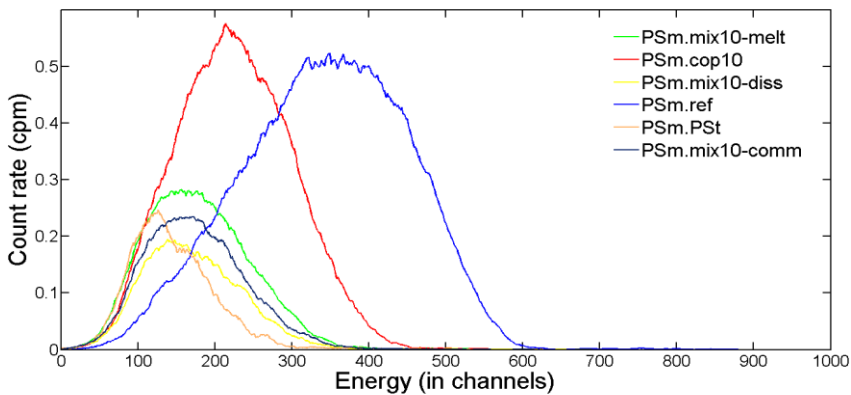
These results prove that when using a copolymer of PS and PVK the energy transmission is better, and, because of this, quenching interferences are lower. Also, it has been observed that a proportion of 10% of PVK is needed in order to obtain an improvement on the detection efficiency results.

6.5. COUNT RATE SPECTRA COMPARISON OF EACH RADIONUCLIDE

The highest detection efficiency and SQP(E) results have been obtained using PSm with a proportion of 10% of PVK. Therefore, in this section, all count rate spectra obtained using PSm of that proportion will be compared with reference spectra. In this way, it will be easy to compare the spectra position on the energy channels axis.

On the one hand, in Figures 17, 18 and 19, it can be observed how PSm.mix10-melt, PSm.mix10-diss and PSm.mix10-comm have a very similar position in the spectrum. Therefore, it can be concluded that the methodology of synthesis of PVK does not affect the position of the spectra obtained what means that similar levels of quenching are present. Moreover, all three are more shifted to high energy channels than it is the spectrum of PSm of only PS (PSm.PSt). This fact confirms that PVK improve the scintillation results.

On the other hand, the spectrum of PSm.cop10 shows a significantly higher energy channel position than other PSm what means that lower quenching interferences are achieved. However, it is still far from reference spectrum of PSm.ref.

Figure 17. Count rate spectra of scintillation measurements of $^{90}\text{Sr}/^{90}\text{Y}$.Figure 18. Count rate spectra of scintillation measurements of ^{241}Am .Figure 19. Count rate spectra of scintillation measurements of ^{14}C .

7. CONCLUSIONS

In summary, it has been checked that PVK can be synthesized easily by polymerization of VK using two different methods: melting and dissolution. The method consisting in dissolve VK in acetonitrile and, later, polymerize the resultant solution, has offered better results.

The evaluation of the scintillation capabilities of PVK conclude that it can not be used as a whole scintillator system. A high luminescence phenomenon observed while using PSm prepared only of PVK is a huge drawback for its use. In addition, quenching interferences are very high and, therefore, detection efficiency values are low, far from reference results.

It has been observed that PSm prepared from mixtures of PS and PVK in proportions of 2% and 10% of PVK offer better results than PSm of only PVK. No luminescence phenomenon is observed, and slightly better detection efficiency results are achieved. Anyway, values obtained are not high enough.

It has been found that if PVK is copolymerized together with polystyrene, quenching interferences are much lower and, therefore, higher detection efficiencies can be achieved. The main hypothesis is that energy transmission between polymers chains is much better when PVK and PS are polymerized together rather than mixed once they are already polymers. Nevertheless, only PSm of copolymer of 10% of PVK have offered significantly higher detection efficiency results achieving values of about 30% for ^{14}C , 156% for $^{90}\text{Sr}/^{90}\text{Y}$ and 84% for ^{241}Am .

Therefore, it is concluded that PVK can be used as primary fluorophore in scintillator system of PSm of copolymer PS/PVK (90:10). In future studies, the ratio of PS/PVK in the copolymer can be optimized in order to achieve even higher detection efficiency results.

As final conclusion, this study has been a promising first step in order to finally use PVK for PSresin preparation and selective radionuclide determination.

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9. ACRONYMS

AIBN	2,2'-Azobis(2-methylpropionitrile)
DCM	Dichloromethane
LS	Liquid scintillation
POPOP	1,4-bis(5-phenyl-2-oxazolyl) benzene
PPO	2,5-dipheniloxazole
PS	Polystyrene
PSm	Plastic scintillation microspheres
PSresin	Plastic scintillation resin
PVA	Polyvinyl alcohol
PVK	Poly (9-vinylcarbazole)
SEM	Scanning electron microscope
VK	9-vinylcarbazole

APPENDICES

APPENDIX 1: DESCRIPTIVE IMAGES

- Image of PVK synthesized from VK's melting and polymerization (left) and polystyrene (right).

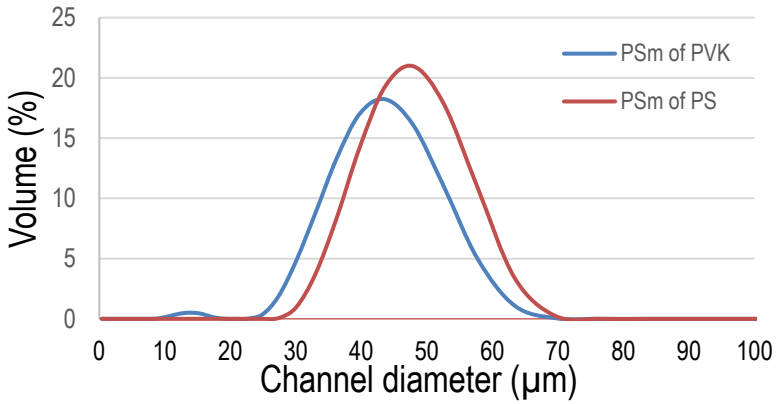


- Image of PVK synthesized from VK's dissolution in acetonitrile and polymerization.



APPENDIX 2: GRANULOMETRIC ANALYSIS

Particle size distribution of PSm of PVK and PS



Particle size distribution of PSm of PS/PVK

