The Synthesis and Characterization of Poly Vinyl Chloride Chemically Modified with C$_{60}$

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Abstract: The fullerenated poly vinyl chloride was synthesized by the addition reaction of azido-substituted poly vinyl chloride with C$_{60}$. Structural characterization carried out using Raman and FTIR spectroscopy confirm the presence of C$_{60}$ chemically bound in the new compound. Also, the photoluminescence properties of fullerenated poly vinyl chloride are considerably changed from those of C$_{60}$

Keywords: Fullerenated poly vinyl chloride, infrared and Raman spectroscopy, photoluminescence

INTRODUCTION

The combination of the unique properties of C$_{60}$ (1) with good processability of polymers through chemical synthesis of fullerenated polymers would open up possibilities for making advanced polymeric materials with new physico-chemical properties.

The tendency of C$_{60}$ to react with other organic groups makes possible its incorporation in various organic polymers. Recently, by different
chemical routes many types of fullerene polymeric derivatives having the polymer chains covalently attached to C$_{60}$ cage have been prepared: i) main-chain fullerene polymer (named also “pearl necklace”); ii) immobilization of fullerenes on polymer solid surface; iii) star-shaped fullerene polymers (known as “flagellenes”); iv) fullerene-end-capped polymers; v) crosslinked polymer fullerene derivatives; vi) side-chain fullerene polymer (often called “pendant chain”) and vii) fullerodendrimer (2, 3). Thus, polystyrene-modified fullerenes have been obtained by bulk or solution radical polymerization (4–7). “Living” polystyrene can be grafted onto C$_{60}$ by anionic polymerization (8–12). A soluble polymer-modified fullerene was prepared by the reaction of linear polystyrene containing azide functional groups with C$_{60}$ (13). Because the azide group is easily introduced in the polymer chain and its reaction with C$_{60}$ can be controlled, this method has been widely used. For example, fullerene-containing poly (alkyl methacrylates) (14) and fullerenated poly (2-hydroxyethyl methacrylate) (15) were synthesized using the cycloaddition reaction of azido-substituted polymer with C$_{60}$.

Another well-known polymer with vast applications in several areas of the materials industry, such as flexible or rigid plastic molds, fibers, films, and laminates, is poly vinyl chloride (PVC). Only a few studies have been reported on C$_{60}$-doped PVC (16, 17). Such a material reveals negative photoconductivity and may have found wide applications in photodetection and radiation measurements (16). To our knowledge, no study regarding the chemical modification of PVC with C$_{60}$ has been carried out.

In the light of above observations, in the present work an attempt to synthesize and to characterize the C$_{60}$-modified PVC has been made. The C$_{60}$-modified PVC was prepared by the addition of C$_{60}$ onto azido-substituted PVC. A priori, this method should allow to the final product to retain the electronic properties characteristics of C$_{60}$ along with the processability of PVC. The vibrational properties of C$_{60}$-modified PVC were investigated by FTIR and Raman spectroscopy. Also, the emission properties of fullerenated PVC were investigated by photoluminescence.

**EXPERIMENTAL**

**Chemicals**

Commercial PVC, obtained by suspension polymerization, without stabilizer or plasticizers, was used after purification by dissolution in tetrahydrofuran followed by re-precipitation from methanol. The K-Wert value of PVC is 59. Sodium azide (NaN$_3$) was from Merck. The C$_{60}$ powder (99.5%) was purchased from Aldrich and used as received. N,N-dimethylformamide, methanol, 1,2-dichlorobenzene, petroleum ether, toluene were from Merck and used without further purification.
Polymer Modifications

The azido-substituted PVC was prepared by adding 1 g NaN₃ to the diluted PVC (1 g PVC in 20 ml N,N-dimethylformamide) for 2.5 hours at 60°C (18). The azide polymer was separated by precipitation in methanol.

The covalent attachment of C₆₀ to azido-substituted PVC was made in dichlorobenzene at 130°C. C₆₀ (0.0082 g) was separately diluted in dichlorobenzene (5 ml) and mixed with an azido-substituted PVC (0.1895 g) diluted in 7 ml dichlorobenzene. The two C₆₀-modified PVC compounds investigated in this work were prepared maintaining constant the concentration of all reactants and varying the reaction time, 6 hours for the first and 8 hours for the second. The crude product was isolated by precipitation in petroleum ether. In order to remove unreacted C₆₀ the powder was re-dissolved in 1,2-dichlorobenzene (solvent for both components C₆₀ and C₆₀-modified PVC) followed by re-precipitation in toluene, solvent only for C₆₀. It is well-known that the color of C₆₀ solution in toluene is violet. For both C₆₀-modified PVC compounds this typical color is not observed.

Measurements

The chemical composition of the all compounds synthesized in this work was obtained using the elemental analysis performed by a multy EA 3100.

Molecular weights were appreciated by gel permeation chromatography (GPC) (Waters 510-type apparatus, tetrahydrofuran as solvent).

The Raman studies were performed at room temperature, under 1064 nm excitation wavelength using a FT Raman Bruker RFS 100 spectrophotometer.

The FTIR spectra were recorded by FT IR Bruker Vertex 70 spectrophotometer in the 4000–400 cm⁻¹ range and 4 cm⁻¹ resolution using KBr pellet techniques.

The photoluminescence (PL) spectra at room temperature were recorded using a Horiba Jobin Yvon Fluorolog 3–22 spectrofluorimeter on powder samples. The excitation wavelength used was 435 nm. The reported PL spectra are not corrected with spectral response of diffraction gratings and quantum efficiency of photomultiplier.

RESULTS AND DISCUSSIONS

The transformation degree of PVC in azido-substituted polymer was verified using the elemental analysis. The results of the elemental analysis are: 37, 62% C; 4, 70% H and 13, 03% N. Taking into account these data an azidation degree of 19, 8% was obtained, confirming the value from literature (18).
To prove the chemical bond between azido-substituted PVC and C_60, the GPC measurements were carried out. The following molecular weights were obtained: 163,300 for azido-substituted PVC, 166,060 for fullerenated poly vinyl chloride obtained after 6 hours reaction time and 168,150 fullerenated poly vinyl chloride obtained after 8 hours reaction time. The graft degree for fullerenated poly vinyl chloride was estimated at 0.79% (6 h reaction time) and 1.38% (8 h reaction time).

The Raman spectrum of azido-substituted PVC (Figure 1A) is dominated by the C-Cl stretching bands group ranging 610–700 cm\(^{-1}\) and CH\(_2\) deformation band near 1432 cm\(^{-1}\). It exhibits also a band at about 2146 cm\(^{-1}\) associated to the azide stretching vibration.

The comparison between the Raman spectra of azido-substituted PVC and the Raman spectrum of fullerenated poly vinyl chloride obtained after 6 hours time reaction (Fig. 1B) reveals the following modifications: i) the intensity of the Raman bands associated with C-Cl stretching situated in the spectral range 610–700 cm\(^{-1}\) decrease in the case of fullerenated PVC; ii) the band situated at 1432 cm\(^{-1}\) also decrease in intensity and shifts to 1438 cm\(^{-1}\); iii) the presence of C\(_{60}\) in fullerenated PVC is confirmed by the four intensively Raman active modes of C\(_{60}\) namely Hg (1), Ag (1), Hg (4) and Ag (2) ("pentagonal pinch" mode) situated at 272, 496, 772 and 1470 cm\(^{-1}\) and finally iv) the enhancement of the band associated to Hg (7) vibrational mode of C\(_{60}\) situated at 1427 cm\(^{-1}\). We notice that the enhancement of the band situated at 1427 cm\(^{-1}\) is not observed in the case of Raman spectrum of azido-substituted PVC/C\(_{60}\) physical mixture. It has to be mentioned that the Raman spectrum of fullerenated PVC obtained after 8 h time reaction could not be recorded. In this case the sample suffers photo-degradation process immediately after it is exposed to the laser radiation (laser was operated at a power of 30 mW).

More information concerning the functionalization of C\(_{60}\) is offered by the FTIR spectra (Figure 2). The FTIR spectrum of azido-substituted PVC (Figure 2A) presents a great number of absorption maxima between 500 and 1500 cm\(^{-1}\), being dominated by the band situated at \(~2112\) cm\(^{-1}\) related to azide group. The shoulder visible at about 638 cm\(^{-1}\) is attributed to the C-Cl stretching vibration mode. The FTIR spectrum of the physical mixture azido-substituted PVC/C\(_{60}\) (weight ratio: 23) (Figure 2D) represent a sum of the two components contributions. It is dominated by the polymer signature, but in the low frequency domain may be easily identified the IR bands of C\(_{60}\) situated at 526 and 575 cm\(^{-1}\). In the case of both fullerenated PVC obtained after 8 or 6 h time reaction, the FTIR spectra (Figure 2B and Figure 2C, respectively) reveals new bands in the spectral range 1600–1750 cm\(^{-1}\). In our opinion this experimental result may be considered as an evidence of the interactions between C\(_{60}\) with azido-substituted PVC.

Another argument which sustains the idea that from the reaction between azido-substituted PVC and C\(_{60}\) results a new compound having optical properties different from those of C\(_{60}\) is given by the photoluminescence. The PL
Figure 1. Raman spectra of azido-substituted PVC (A), fullerenated poly vinyl chloride (B) and C_{60} (C). *Peaks attributed to C_{60}.

Spectrum of fullerenated PVC (Fig. 3 solid line) recorded at 435 nm excitation wavelength reveals a wide emission band with a maximum at ~600 nm different from that of C_{60} powder with maximum at about 725 nm (Figure 3 dot line). Also, for comparison is presented the PL spectrum of the physical
Figure 2. IR spectra of: azido-substituted PVC (A), fullerenated poly vinyl chloride obtained after 8 hours time reaction (B), fullerenated poly vinyl chloride obtained after 6 hours time reaction (C), azido-substituted PVC/C₆₀ physical mixture (D) and C₆₀ (E). *Peaks attributed to C₆₀
mixture azido-substituted PVC/C₆₀ (weight ratio: 23) (Figure 3 dash line) with maximum at ~510 nm obtained at the same excitation wavelength. We mention that a similarly emission was observed also in the case of azido-substituted PVC. In our opinion the absence of the C₆₀ signature in the PL spectrum of the physical mixture is due to the large weight ratio between the two components.

CONCLUSIONS

We have studied by Raman scattering, IR absorption and photoluminescence the fullerenated polyvinyl chloride. The modifications observed in the vibration and emission spectra, the appearance of new IR bands between 1600–1750 cm⁻¹ and the wide band with maximum at 600 nm in the PL spectrum, respectively sustained the hypothesis that from the addition reaction between azido-substituted PVC and C₆₀ results a new fullerenated PVC compound.

REFERENCES


Figure 3. PL spectra of fullerenated poly vinyl chloride (solid line), azido-substituted PVC/C₆₀ physical mixture (dash line) and C₆₀ (dot line), λexc = 435 nm.