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Synthesis and optical properties of water-soluble poly(vinylpyrrolidone) - modified fullerene C_{60}

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Summary

The effect of fullerene on the radical polymerization of N-vinylpyrrolidone with lauroyl peroxide in toluene was investigated kinetically. C_{60} was found to act both as inhibitor and as retarder because the polymerization rate and the molecular weight of resulting poly(vinylpyrrolidone) is decreasing with the increase of the fullerene concentration (0-6.94 x 10^{-4} mol l^{-1}). The water-soluble poly(vinylpyrrolidone)-modified fullerene C_{60} compound was characterized by differential scanning calorimetric, Infrared and Raman spectroscopy, UV absorption and photoluminescence. Based on the results obtained by optical measurements, it is argued that by the covalent attachment of the polymeric radicals to fullerene cage the extended electronic conjugation system of the C_{60} is broken leading to the appearance of a polyene structure.

Introduction

The unique physical and chemical properties of C_{60} [1] have driven researchers to find more and more application for them. In the last years, the interest for the potential biological and biomedical applications of C_{60} [2] such as: imaging probes [3], antioxidants [4, 5] and drug carries [6] has increased. Hybrid materials formed by C_{60} with proteins may be a new storing structure for novel pharmacological substances [7]. From the practical point of view these applications require the solubilization of C_{60} in water. Several attempts have been made to overcome the natural repulsion of C_{60} for water. The most widely used methodologies are: formation of water soluble host-guest complexes [8-11]; suspension with the help of co-solvents [12-14]; solubilization by surfactants [15-17]; chemical functionalization for the introduction of solubilizing appendages [18]. Recently researches on the C_{60} complexed or derivatized with hydrophilic polymers have intensified since these polymers are soluble in water. Thus poly(ethyleneoxide)-modified C_{60} have been prepared with a precursor possessing mono- or di-azido end groups [19, 20]. C_{60}-containing poly(ethyleneoxide) was also synthesized from mono-or di-amino terminated poly(ethyleneoxide) [21]. "Living" poly(ethyleneoxide) can be grafted onto C_{60} [22].

Poly(vinylpyrrolidone) (PNVP) is another well known non-toxic, biocompatible and hydrophilic polymer remarkable for its biomedical properties. C_{60} being a strong electron acceptor form complex with PNVP [23]. Such a structure may have direct implication for the biological effect, acting on the lipid component of virus membranes [24, 25]. Another way to obtain a more stable structure than the complex mentioned above, consist in the chemical functionalization of C_{60} with polymeric chains. 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 [26, 27]. A priori, the tendency of C_{60} to react with other organic groups and the radical reactivity of the N-vinylpyrrolidone (NVP) would make possible a direct covalent bonding of polymeric radicals to fullerene cage. Fullerene C_{60} is reported to react with styrene and other olefins by bulk or solution radical polymerization to form polystyrene-C_{60} compounds [28-30], but is also known to quench radicals and inhibit polymerization. We note that to our knowledge only one paper was published about the C_{60}-NVP copolymer [31]. But in this case a dimethylfulleropyrrolidine was chose as a starting material.

In this paper we report a covalent attachment of PNVP to C_{60} cage achieved by the radical polymerization of NVP in the presence of C_{60} and lauroyl peroxide as an initiator. According to our expectations, the method leads to a polymer-modified fullerene compound soluble in water. Inhibition and retarder behavior of C_{60} in the polymerization reaction is explored by simple dilatometric experiments. A kinetic model is discussed, too. Using differential scanning calorimetric, Infrared and Raman spectroscopy, UV absorption and photoluminescence we show that the synthesized water-soluble compound, poly(vinylpyrrolidone)-modified fullerene C_{60} (PNVP-C_{60}), contains polyene structures formed by the breaking of the extended electronic conjugation system of fullerene after the covalent attachment of polymer chains to C_{60} molecule.

Experimental

Materials

NVP, lauroyl peroxide (LP), toluene (T) and ethylic ether (EtEt) of synthetic grade were purchased from Merck. NVP was distilled under vacuum at 88°C and 9 mmHg. The initiator, LP, was recrystallized from ethanol. The solvent, T, was distilled at 110°C. The non-solvent, EtEt, was used without further purification. The C_{60} powder from Aldrich was used as received.

Polymerization

In a typical procedure mixture of ($[NVP] = 3.12\ mol\ l^{-1}$) - C_{60} - ($[LP] = 2.6 \times 10^{-2}\ mol\ l^{-1}$) - T dosed in polymerization tubes or in dilatometer were conditioned through nitrogen bubbling and then placed in thermostatic baths at 70°C. The C_{60} concentration and polymerization time were varied to observe polymerization characteristics. The crude product was isolated by precipitation in non-solvent and afterward filtered, washed and dried until to constant weight. We notice that the initial color of C_{60} solution in T was violet. After separation of the precipitate, the liquid phase remains colorless sustaining the hypothesis that during the polymerization reaction of NVP the properties of fullerene are modified.

Methods

The polymerization kinetic was studied by dilatometric method. Molecular weights of the samples obtained in different experimental conditions were obtained by viscosimetric measurements. The intrinsic viscosities of solutions were measured at 30°C in water using a Ubbelohde type capillary viscometer. The thermal behavior of PNVP-C_{60} powder was determined by differential scanning calorimetric (DSC) using a Linseis 2005, up to 700°C.

The FTIR spectra were obtained using a Shimadzu 8900 spectrophotometer in the 4000-400 cm^{-1} range and 2 cm^{-1} resolution. The Raman studies were performed at room temperature, under 1064 nm excitation wavelength using a FT Raman Bruker RFS 100 spectrophotometer.

Ultraviolet absorption spectra were recorded in the range 200-350 nm using a Jasco V550 spectrophotometer with integrating sphere. The photoluminescence (PL) spectra at room temperature were recorded using a Horiba Jobin Yvon Fluorolog 3-22 spectrofluorimeter. The excitation wavelengths used were 335, 365, 400 and 435 nm and the emission was monitored between 350…655, 380…715, 415…785 and 450…850 nm, respectively.

Results and discussion

In order to ascertain whether C_{60} acts as inhibitor and/or retarder for "in situ" radical polymerization of NVP, simple dilatometric experiments were conducted at 70°C. Figure 1 shows the extent of monomer conversion as a function of time. The concentration of monomer ([NVP] = 3.12 mol l^{-1}) and the initiator [LP] = 2.6 x 10^{-2} mol l^{-1}) were maintained constant, while the concentration of the C_{60} was varied in the range 2 x 10^{-4} - 6.94 x 10^{-4} mol l^{-1}. Polymerization of NVP without fullerene under the same condition was also conducted for comparison. Figure 2 presents the dependence of induction time on C_{60} concentration. As might be expected the induction period increases with increased concentration of C_{60}. So, C_{60} acts like a radical absorber reacting with primary radicals from LP faster than with monomer. Therefore, the NVP polymerization occurs only after sufficient C_{60} is consumed to permit the reaction of primary initiator radicals with NVP. This means that in radical polymerization of NVP, C_{60} behaves at least as an inhibitor. In order to bring out the role played by the C_{60} in the NVP polymerization we have determined by dilatometry the polymerization rates for the investigated system (Figure 3). Because the polymerization rate highly decreases when C_{60} is present in the polymerization mixture it seems quite reasonable to suppose that C_{60} acts also as retarder in the NVP polymerization.

Thus, in the light of the above observations upon the NVP polymerization conducted at low conversion in the presence of C_{60}, we may write a polymerization mechanism, taking into account: the initiation, propagation, the addition of polymer radicals to C_{60} and termination by combination steps.

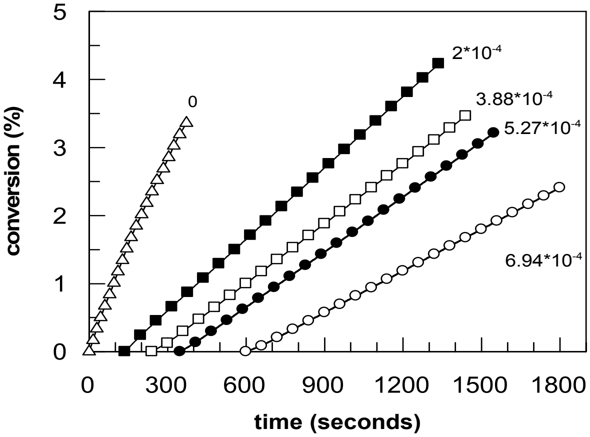


Figure 1 Dependence of conversion on time for the LP - initiated radical polymerization of NVP in absence and in the presence of fullerene. The monomer and initiator concentrations were kept constant, 3.12 mol l^{-1} and 2.6 x 10^{-2} mol l^{-1}, respectively. The concentration of C_{60} was varied in the range 2 x 10^{-4} - 6.94 x 10^{-4} mol l^{-1}.

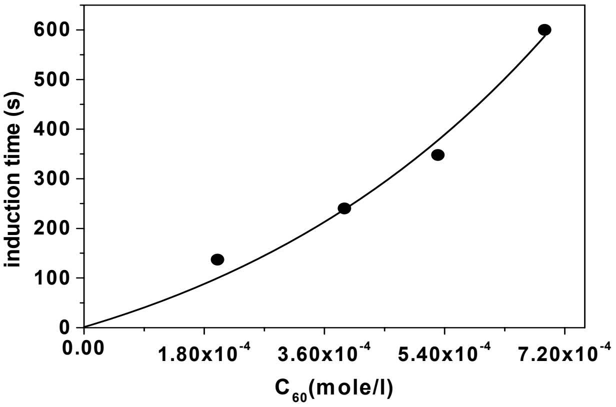


Figure 2 The dependence of the induction time on C_{60} concentration in the LP - initiated radical polymerization of NVP.

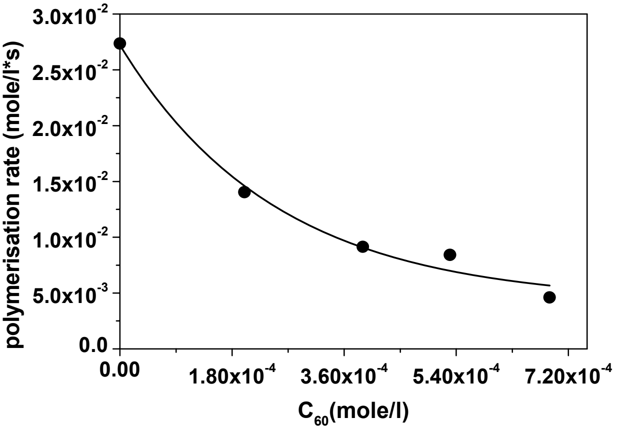
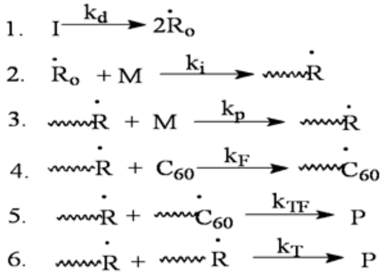


Figure 3 The polymerization rate dependence on C_{60} concentration in the LP - initiated radical polymerization of NVP.

In the proposed reaction scheme k_d is the rate constant of dissociation of initiator, k_i is the rate constant for monomer, association, k_p is the propagation rate constant, k_F is the rate constant for addition of polymer alkyl radicals to C_{60}, k_{TF} is the rate constant for the termination of polymer alkyl radicals by combination with fullerene radicals and k_T is the termination rate constant of polymer alkyl radicals by combination between them.



Scheme 1 Reaction scheme for radical polymerization of NVP in the presence of C_{60}.

In the reaction scheme, I, M and P designate the un-dissociated initiator, monomer and terminated polymers, respectively; the R_0, R and C_{60} with dot surmounting are the initiator, monomer and fullerene radicals, respectively.

For the kinetic model we made de following simplifications:

1. We have neglected the chain transfer reactions towards the monomer because they have a small contribution in the estimation of polymerization rate compared with the propagation reactions [32];
2. The polymer radicals are attached to the C_{60} cage the new radicals formed in this stage are involved only in the termination reactions;
3. The termination reactions between C_{60} radicals have been neglected due to kinetic improbability.

Starting from the hypothesis that the (R_i) radicals are generated and consumed with the same rate, we may write:

$$R_i = k_{TF} \cdot \dot{C}_{60} \cdot \dot{R} + k_T \cdot \dot{R}^2 \qquad \textbf{(1)}$$

The solution of the equation (1) gives the dependence between the propagating radicals concentration and the C_{60} radicals concentration:

$$\dot{R} = \frac{\sqrt{(k_F \cdot \dot{C}_{60})^2 + 4 \cdot k_T \cdot R_i} - k_F \cdot \dot{C}_{60}}{2 \cdot k_T}$$

Imposing the steady-state condition for the C_{60} radicals:

$$\dot{C}_{60} = \frac{k_F \cdot C_{60}}{k_{TF}} \qquad \textbf{(2)}$$

In this context the polymerization rate in the presence of C_{60} (R_p) is:

$$\frac{R_{p0}}{R_p} = \frac{2 \cdot R_i^{0.5} \cdot k_T^{0.5}}{\sqrt{k^2_F \cdot C^2_{60} + 4 \cdot k_T \cdot R_i} - k_F \cdot C_{60}} \qquad \textbf{(3)}$$

Notating $A = 2 \cdot R_i^{0.5} \cdot k_T^{0.5}$ and $B = k_F \cdot C_{60}$, we transforms into:

$$\frac{R_{p0}}{R_p} = \frac{A}{\sqrt{A^2 + B^2} - B} \tag{4}$$

Thus:

$$B = \frac{A}{2} \cdot \left(\frac{R_{p0}}{R_p} - \frac{R_p}{R_{p0}}\right)$$

Taking into consideration that A value is a constant, easily results the dependence of C_{60} concentration on the polymerization rate (R_{p0}) and R_p:

$$\left(\frac{R_{p0}}{R_p} - \frac{R_p}{R_{p0}}\right) = \frac{C_{60}}{K} \tag{5}$$

The equation (5) is a linear one having the slope 1/K, where:

$$K = \frac{k_T^{0.5} \cdot R_i^{0.5}}{k_F}$$

The validation of the proposed kinetic model, demands that the graphical representation of the experimental value $\left(\frac{R_{p0}}{R_p} - \frac{R_p}{R_{p0}}\right)$ on C_{60} concentration must obey equation (5) and from Figure 4 we see that it is exactly the case.

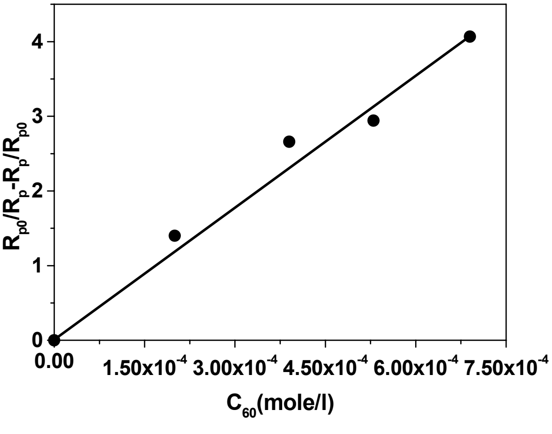


Figure 4 The dependence of $\left(\frac{R_{p0}}{R_p} - \frac{R_p}{R_{p0}}\right)$ experimental values on C_{60} concentration in the LP - initiated radical polymerization of NVP.

The linear dependence observed in Figure 4 may be an argument for the validation of kinetic model. From experimental values, K was calculated as being equal with 1.75×10^{-4} ($l\ mol^{-1}$). If we accept that the initiation rate has the following value $R_i \approx 10^{-6}$ ($mol\ l^{-1}\ s^{-1}$) and $k_T \approx 10^9$ ($l\ mol^{-1}\ s^{-1}$) [33] we obtain $k_F \approx 1.8 \times 10^5$ ($l\ mol^{-1}\ s^{-1}$). This value is comparable with those obtained for propagation and termination constants.

Based on the same kinetic model we can anticipate the ratio between the number average degree of polymerization in the absence ($GP_{n,0}$) and in the presence (GP_n) of C_{60}, respectively. The GP_n is described by:

$$\frac{1}{GP_n} = \frac{R_t}{R_p} = \frac{k_{TF} \cdot \dot{R} \cdot \dot{C}_{60} + k_T \cdot \dot{R}^2}{k_p \cdot M \cdot \dot{R}} \qquad \textbf{(6)}$$

Substituting in this relation the concentration of propagating radicals and that of C_{60} radicals with the expressions found above, we obtain:

$$\frac{1}{GP_n} = \frac{\sqrt{k^2{}_F \cdot C^2{}_{60} + 4 \cdot k_T \cdot R_i} + k_F \cdot C_{60}}{k_p \cdot M \cdot 2} \qquad \textbf{(7)}$$

The $GP_{n,0}$ is given by:

$$\frac{1}{GP_{n,0}} = \frac{k_T \cdot \dot{R}^2}{k_p \cdot M \cdot \dot{R}} = \frac{(k_T \cdot R_i)^{0.5}}{k_p \cdot M} \qquad \textbf{(8)}$$

Dividing the (8) by (7) the next relation is obtained:

$$\frac{GP_n}{GP_{n,0}} = \frac{(k_T \cdot R_i)^{0.5} \cdot 2}{\sqrt{k^2{}_F \cdot C^2{}_{60} + 4 \cdot k_T \cdot R_i} + k_F \cdot C_{60}} \qquad \textbf{(9)}$$

Maintaining the notation for A and B, equation (9) transforms into:

$$\frac{GP_n}{GP_{n,0}} = \frac{A}{B + \sqrt{A^2 + B^2}} = R$$

Analyzing this relation we may found the dependence between B, A and R. Thus:

$$\frac{(1 - R^2)}{R} = \frac{2 \cdot B}{A}$$

Maintaining A as constant, we can easily determine the dependence between R and C_{60} concentrations. $K = 1.75 \times 10^{-4}$ (l mol^{-1}), value obtained experimental.

$$\frac{(1 - R^2)}{R} = C_{60} / K$$

Knowing the values for K and C_{60} concentration, respectively, we can calculate the ratio between the $GP_{n,0}$ and GP_n (Table 1). One has to mention that the PNVP-C_{60} is a totally soluble in water compound. This result sustain the hypothesis that during the polymerization reaction of NVP, the structure and also the properties of C_{60} added are modified by the covalent attachment of polymer chains. The kinetic model accepts the coexistence of two types of polymers: PNVP homopolymer and PNVP-C_{60}. For determining their viscosity average degree of polymerization (GP_v) we can use the experimentally obtained values of the intrinsic viscosity ([η]) and viscosimetric constants $K = 14 \times 10^{-3}$ and $a = 0.7$ calculated for PNVP [34].

Table 1 Characteristics of various PNVP-C_{60} obtained by polymerization of NVP in the absence and in the presence of fullerene (at different concentration). The solution polymerization was carried out in toluene at 70°C, using LP as initiator.

Sample no.	C_{60} concentration (mol l^{-1})	Yield (%)	$(\frac{GP_n}{GP_{n,0}})^*$	[η] (dl g^{-1})	M_v	$(\frac{GP_v}{GP_{v,0}})^{**}$
1	0	3.5	1	0.065	5900	1
2	2×10^{-4}	4.23	0.58	0.105	12800	2.05
3	3.88×10^{-4}	3.36	0.38	0.085	9592	1.50
4	6.94×10^{-4}	2.4	0.24	0.069	7120	1.08

* calculated; ** measured

As shown in Table 1, the $GP_n/GP_{n,0}$ ratio decreases with the increase of the C_{60} concentration. This variation is suggested by the mathematical model, too. One mention that the PNVP-C_{60} presents a greater viscosity average molecular weight (M_v) than PNVP homopolymer synthesized in the same reaction conditions. Such a result may be explain only if we accept that multiple additions of polymeric radicals to the C_{60} cage are leading to a star structure, already reported in the case of polystyrene [35] and poly(vinylacetate) [36] chains covalently attached to a C_{60} cage.

In the following, different properties of PNVP-C_{60} are investigated by thermal and opto-spectral techniques. As it is show in the Figure 5 the DSC spectrum of PNVP-C_{60} (curve 2) is different from the PNVP parent one (curve 1). The endothermic peak at about 170°C, characteristic for PNVP, is much larger in the case of PNVP-C_{60} due to the presence of species with different structures and number average degree of polymerization in this compound.

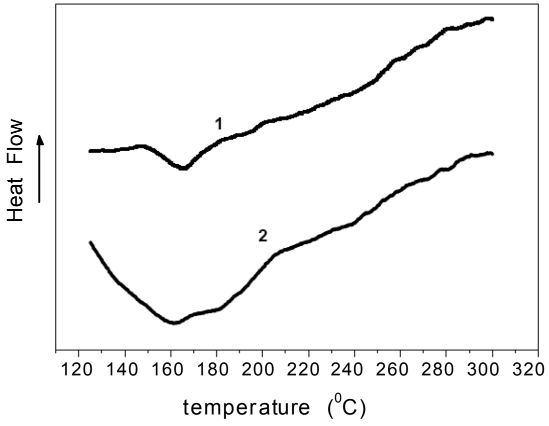


Figure 5 DSC spectra of:
1) PNVP parent and
2) PNVP- C_{60}.

Structural characterization of the PNVP-C_{60} is carried out using IR and Raman methods. For comparison in Figure 6 are presented the IR spectra of PNVP parent (spectrum 3), PNVP/C_{60} physical mixture (spectrum 2) and PNVP-C_{60} (spectrum 1). In the case of IR spectrum for the physical mixture, the band situated at 525 cm^{-1} represents the C_{60} signature as individual molecule. This band disappears in the IR spectrum of PNVP-C_{60} sustaining the hypothesis that the covalent attachment of polymeric chains to the C_{60} cage has as the result the modification of C_{60} structure.

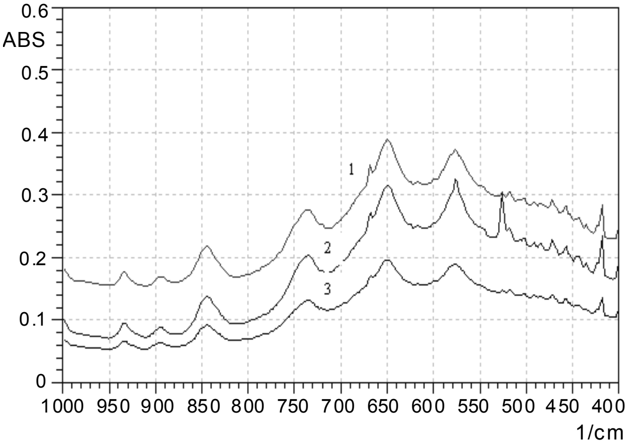


Figure 6 IR spectra for: 1) PNVP-C_{60}, 2) PNVP/C_{60} (physical mixture) and 3) PNVP parent.

In the Raman spectrum of PNVP-C_{60} (Figure 7) the four intense Raman active modes of C_{60} as individual molecule namely Hg (1), Ag (1), Hg (4) and Ag (2) ("pentagonal pinch" mode) situated at 272, 496, 772 and 1470 cm^{-1} are not observed, this being basically similar with that of the parent PNVP. Most probably this similarity is due to the overwhelming contributions of NVP units in the PNVP-C_{60} structure.

A possible explanation for the absence of the C_{60} signature in the Raman spectrum of PNVP-C_{60} could be the following: during the radical polymerization of NVP in the presence of C_{60}, propagating polymeric radicals are covalent linked to C_{60} cage distorting the molecular symmetry and breaking the extended electronic conjugation system of the C_{60}. In this way, multiple additions of the propagating polymeric radicals to the C_{60} cage are leading to the formation of conjugated regions or polyene structures. We note that a Raman band situated at ~1600 cm^{-1} was associated to C=C stretch in conjugated regions formed in the individual micron diameter polystyrene particles isolated in a visible wavelength radiation trap [37]. Consequently, we think that the new weak band which appears at ~1595 cm^{-1} in the Raman spectrum of PNVP-C_{60} (spectrum B) is an argument for the formation of the polyene regions.

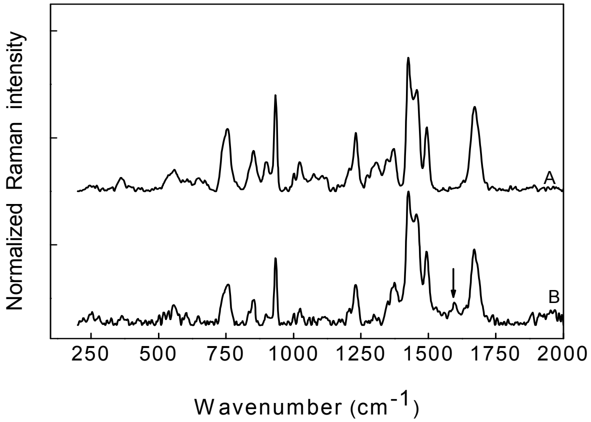


Figure 7 Raman spectra of PNVP parent (A) and PNVP-C_{60} (B) recorded at 1064 nm excitation wavelength.

UV absorption and photoluminescence studies give the convincing proof that by radical polymerization of the NVP in the presence of fullerene was formed a new compound which contains the polyene cromophore. Thus, in the UV absorption spectra of PNVP-C_{60} (obtained at different conversion) presented in Figure 8, characteristic peaks of C_{60} as individual molecule are not observed.

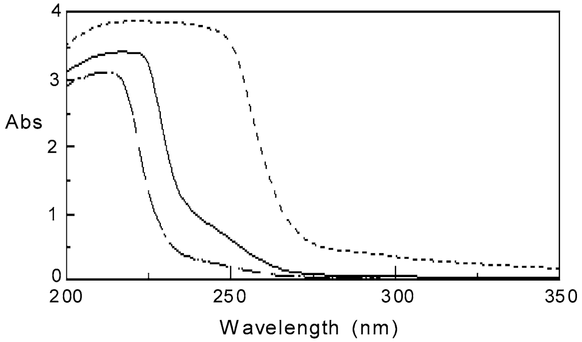


Figure 8 UV absorption spectra of PNVP-C_{60} powders obtained at different conversions: 30% (dash line), 20% (solid line) and 4% (dot line).

The PL spectra of the PNVP-C_{60} powder recorded at different excitation wavelengths (Figure 9) exhibits a wide band with the maximum at about 535 nm. Such a green emission was already identified in polystyrene films exposed to UV radiation [38] and for individual micron diameter polystyrene particles illuminated with visible radiation in an optical trap [39] and associated to the polyene cromophore. A band peaking around 535 nm is observed also in the PL spectrum of PNVP-C_{60} water solutions (Figure 10) obtained at 435 nm excitation wavelength.

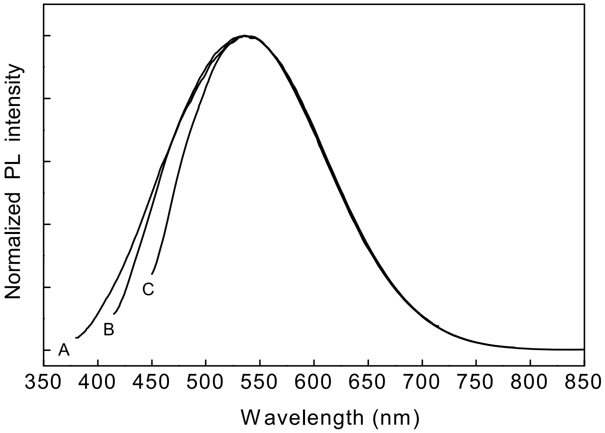


Figure 9 Photoluminescence spectra of PNVP-C_{60} powder at different excitation wavelengths: 365 nm (A), 400 nm (B) and 435 nm (C).

Compared with the emission of the parent PNVP water solution, the emission of the PNVP-C_{60} water solution is red shifted supplying the presumption that by the radical polymerization of NVP in the presence of C_{60} a new compound characterized by a green emission is formed. In the case of polymer water solution, the intensive Raman line of water situated at about 3300 cm^{-1} is superposed onto PL spectrum. In the inset is shown the PL spectrum of PNVP-C_{60} water solution at 335 nm wavelength excitation. It reveals also the broad band emission with the maximum around 535 nm.

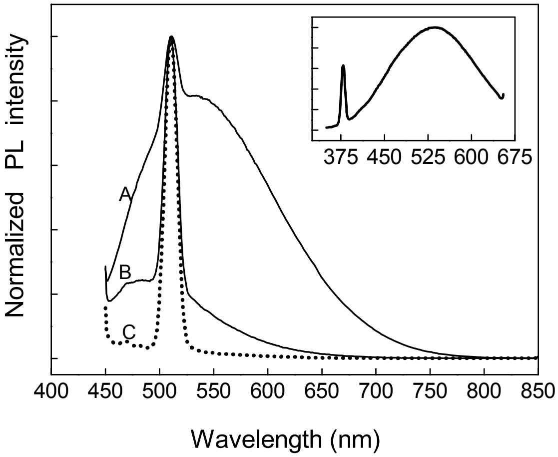


Figure 10 Photoluminescence spectra of PNVP-C_{60} (A) and PNVP parent (B) in water at 435 nm excitation wavelength. The emission spectrum of water filled cuvette (C) is also shown. In the inset is presented the photoluminescence spectrum of PNVP-C_{60} in water at 335 nm excitation wavelength.

It has to be mentioned that this green emission featuring the PL spectra of the PNVP-C_{60} as powder or water solution preserves its shape and position when the excitation wavelength is changed.

Conclusions

This paper reports new results concerning the synthesis and the characterization of a water soluble compound based on PNVP and fullerene C_{60}. The C_{60} has been added in the polymerization reaction of NVP initiated by LP and its influence has been investigated. Using simple dilatometric experiments, we found that C_{60} acts both as inhibitor and as retarder. A kinetic model was proposed and validated by the experimental data. The DSC, IR, Raman, UV absorption and PL studies sustain the hypothesis that by direct covalent bonding of polymeric radicals to fullerene cage, the extended electronic conjugation system of the C_{60} is broken, leading to the appearance of a polyene structures. Concluding, the PNVP-C_{60} is a compound soluble in water which may have direct implication for the biomedical applications.

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References

1. Kroto HW, Allaf A, Balm SP (1999) Chem.Rev. 91:1213
2. Bosi S, Da Ros T, Spallato G, Prato M (2003) Eur. Poly. Med. Chem. 38:913
3. Bolskar RD, Benedetto AF, Husebo LO, Price RE, Jackson EF, Wallace S, Wilson LJ, Alford JM (2003) J. Am. Chem. Soc. 125:5471
4. Chen YW, Hwang KC, Yen CC, Lai YL (2004) Am. J. Physiol. Regul. Integr. Comp. Physiol. 287:R21
5. Dugan LL, Gabrielsen JK, Yun SP, Lin TS, Choi DW (1996) Neurobiol. Dis. 3:129
6. Zakharian TY, Seryshev A, Sitharaman B, Gilbert B, Knight V, Wilson LJ (2005) J. Am. Chem. Soc. 127: 12508
7. Murakami H, Okusa Y, Kiyonaka S, Hamachi I, Shinkai S, Nakashima N (2000) Chem. Lett. 46

8. Samal S, Choi BJ, Geckeler KE (2000) Chem. Commun. 1373
9. Samal S, Geckler KE (2000) Chem. Commun. 1101
10. Wang J, Bodige SG, Watson WH, Gutsche CD (2000) J. Org. Chem. 65:8260
11. Ala-Kleme T, Maki R, Laaksonen P, Haapakka K (2002) Analytica Chimica Acta 472:83
12. Andrievsky GV, Klochkov VK, Bordyuh AB, Dovbeshko GI (2002) Chem. Phys. Lett. 364:8
13. Scharff O, Risch K, Carta-Abelmann L, Dmytruk IM, Bilyi MM, Golub OAA, Khavryuchenko V, Buzaneva EV, Aksenov VL, Avdeev MV, Prylutskyy YI, Durov SS (2004) Carbon 42:1203
14. Deguchi S, Alargova RG, Tsujii K (2001) Langmuir 17:6013
15. Petrossyan NO, Klochkov VK, Andrievsky GV (1997) J. Chem. Soc., Faraday Trans. 93:4343
16. Ungurenasu C, Airinei A (2000) J. Med. Chem. 43:3186
17. Sushko ML, Tenhu H, Klenin SI (2002) Polymer 43:2769
18. Tabat Y, Murakami Y, Ikada Y (1997) Fullerene Sci. Technol. 5:989
19. Hawker CJ, Saville PM, White JW (1994) J. Org. Chem. 59:3503
20. Huang XD, Goh SH, Lee SY (2000) Macromol. Chem. Phys. 201:2660
21. Delpeux S, Benguin F, Manolova N, Rashkov I (1999) Eur. Polym. J. 35:1619
22. Ederle Y, Mathis C, Nuffer R (1997) Synth. Met. 86:2287
23. Zgonnik VN, Vinogradova LN, Melenevskaya EYu, Khachaturov A, Klenin SI (1998) Mol. Mater. 11:101
24. Piotrovsky LB, Kiselev OI (2005), Fullerenes, Nanotubes and Carbon Nanostructures 12:397
25. Sirotkin AK, Zarubaev VV, Poznyiakova LN, Dumpis MA, Muravieva TD, Krisko TK, Belousova IM, Kiselev OI, Piotrovsky LB (2006) Fullerenes, Nanotubes and Carbon Nnaostructures 14:327
26. Dai L (1999) Polym. Adv. Technol. 10:357
27. Wang C, Guo ZX, Fu S, Wu W, Zhu D (2004) Prog. Polym. Sci. 29:1079
28. Stewart D, Imrie CT (1996) Chem. Commun. 1383
29. Cao T, Weber SE (1996) Macromolecules 29:3826
30. Ford WT, Graham TD, Mourey TH (1997) Macromolecules 30: 6422
31. Iwamoto Y, Yamakoshi Y (2006) Chem. Commun. 4805
32. Berger K, Meyehoft C (1989) Polymer Handbook 3rd edition, ed. by Brandrup J, Immergut EH, Wiley & Sons, New York, pp. II/76
33. Pavlov GM, Nazarova OV, Ebel C, Mikhailova NA, Zaitseva II, Bokov SN (2005) Russian Journal of Applied Chemistry 78:130
34. Kurata M, Tsunashima Y (1989) Polymer Handbook 3rd editiond. by Brandrup J, Immergut EH, Wiley & Sons, New York, pp. VII/18
35. Samulski ET, DeSimone JM, Hunt MO Jr., Menceloglu YZ, Jarnagin RC, York G, Labat KB, Wang H (1992) Chem. Mater. 4:1153
36. Seno M, Maeda M, Sato T (2000) J. Polym. Sci. Part A: Polym. Chem. 38:2572
37. Crawford KD, Hughes KD (1998) J. Phys. Chem. B 102: 2325
38. Simons JK, Chen JM, Taylor JW, Rosenberg RA (1993) Macromolecules 26: 3262
39. Crawford KD, Hughes KD (1997) J. Phys. Chem. B 101:864