

Synthesis of polyvinyl pyridine/C60 conjugates in supercritical carbon dioxide*

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(Received; 5 Jun 2007 and Accepted; 25 Oct 2007)

Abstract

In the present investigation efforts have been made to synthesis polyvinyl pyridine (PvPy) /C60 conjugates through 2, 2-azobisisobutyronitrile (AIBN) initiated insitu polymerization of PvPy in $scCO_2$. The process of synthesis was monitored under different reaction conditions ranging 1200-1800psi, 60-90 °C over 6 hours. The progress of polymerization was monitored rheoviscometrically. The concentration of PvPy and AIBN ranging $6.95-20.85 \times 10^{-3}$ and $304.50-931.50 \times 10^{-3}$ afforded PvPy/C60 conjugates in the yield (%) ranging 10.30-48.8. Selected PvPy/C60 conjugates were characterized through UV-VIS spectra, scanning electron microscopy, gel permeation chromatography and solution rheoviscometry.

Keywords: Supercritical carbon dioxide, Synthesis, C60/ polyvinyl pyridine conjugates, Rheoviscosity, Spectra, Electron microscopy.

1. INTRODUCTION

C60 a representative of the fullerene family has attracted much attention as a nanostructured material because of its unique physical and chemical properties. However, its poor solubility and process ability are the obstacles for its various nanotechnological applications in medicine (Ford, 1999), superconductivity and non-linear optics (Wang, 2004). In order to overcome the disadvantages, many methods for the chemical modification based on solubilization of C60 through chemical modification, by introduction of surfactants, encapsulation in polymer micelles have been reported (Geckeler, 2004, Mountrichas, 2005). Incorporation of C60 into the polymer chain has been recognized as a simple means of combining the properties of C60 with macromolecular characteristics, such as mechanical strength and

good process ability and the resulting derivatives may refer as “macromolecular fullerenes”. These Macromolecular fullerene derivatives are synthesized through either of direct copolymerization of fullerenes with monomers in presence of radical initiators, functionalization of fullerenes to give a polymerizable monomer and then use this monomer to conduct copolymerization with other monomers and or reacting functionalized polymers with fullerenes (Geckeler, 2004, Mountrichas, 2005). Since past few years, a variety of methods were developed to synthesize macromolecular fullerenes (Shi, 1992, Wang, 2004). Among such methods, free radical polymerization of vinyl monomers in presence of C60 has attracted much attention due to its mild reaction conditions.

The major technical challenge in the synthesis of C60/polymer conjugates through free radical polymerization lies in the radical inhibitory action

of C60. High electrophilicity of C60 makes multiple additions of the electron-deficient organo-radicals, such as benzyl and tert-butyl radicals, possible to the fullerenic double bonds. Rate constants for the addition reaction of the alkyl radicals onto C60 were reported to be 10^7 - 10^9 $\text{m}^{-1}\text{s}^{-1}$, much higher (10^5 times) than those for the propagation of polymer or oligomer chain-end radicals with monomers during the free-radical polymerization of styrene and methylmethacrylates. Therefore, the radical initiators are consumed in the early stage of polymerization by multiple additions onto C60, leading to formation of highly substituted C60 derivatives (Kuo et al 2001).

Recently PMMA modified C60 and C70 compositions through three different methodologies were prepared (Kuo et al 2001, Sun et al 1996). Fullerenes were incorporated to the PMMA chains either at the stage of the initiation of monomer polymerization with two initiators of different structure or by the covalent linkage of C60 through a reaction with the amino end-groups of PMMA, and or by the entering of fullerene in the state of a charge transfer complex into the reaction mixture. Such synthesis methods not only involve toxic, flammable and costly solvents as a reaction medium but also cause problem in separation and isolation of the products from reaction medium. With advancements in chemical technology, a novel method of synthesis has been introduced based on supercritical solvents as reaction media. In this connection, a variety of supercritical fluids has come into picture, particularly supercritical carbon dioxide (scCO_2) has non toxic, non flammable and a cost effective alternatives to conventional solvents. Since past few years, scCO_2 (Bhullar, 2007).

Realizing the radical inhibitory action of C60 during free radical polymerization, in the present investigation efforts have therefore been made to achieve the PvPy- C60 conjugates with enhanced molecular mass through optimizing the concentrations of AIBN, VPy, time in combination with supercritical conditions. Selected PvPy- C60 conjugates were characterized through Uv-Vis spectra and Rheoviscometry.

2. MATERIAL AND METHODS

2.1. Starting materials

Fullerene C60 (99.5%) was purchased from Ms SES research Texas, USA Vinyl pyridine monomer was purchased from Across Chemicals USA.

The inhibitor content of VPy was extracted into aqueous solution of sodium hydroxide (10% w/v), was followed by repeated washings with distilled water. The fraction boiling at 79-82 °C /29 mm (λ max: 295.0, density: 0.975) was collected and used. The other chemicals and solvents were locally purchased and used without further purification.

Uv-vis spectra were recorded over Genesis 10 Thermo Spectronic Spectrophotometer in methanol. The Rheoviscometry measurements were carried out in methanol on a Nach Hoppler Viscometer Germany. Viscosity was derived from the resistance against the solution of corresponding caged polymers with their homopolymer solutions as control. The time when the ball sank 30 mm deep in the cuvette was measured (Gombos, 2005). Gel permeation chromatography was executed electron micrographs of gold coated, samples were scanned at 4.00KX over LEO-435. (Cooper, 2000).

2.2. Synthesis of C60/PvPy conjugates

PvPy/C60 conjugates was synthesized in a stainless steel high pressure reactor (100 cm^3). Reactor was charged with required quantities of monomer, AIBN, and C60. Carbon dioxide (99.99%) was delivered directly to the reaction cell at desired pressure. The system pressure was measured by a pressure gauge. The temperature inside the cell was measured by an industrial insulated thermocouple that was provided and displayed on PID temperature controller. The reactor was heated with an electrical heating tape wrapped around the exterior of the cell. The cell was initially pressurized with carbon dioxide and then gradually heated within a defined temperature range to obtain desired pressure. The reaction mixture was refluxed in scCO_2 for definite time. The cell was cooled to ambient temperature and the CO_2 was vented into dichloromethane. The cell was opened to give crude mass of product ranging from semisolid to solid state. The isolation and separation of conjugates were carried out according to the procedure was reported earlier. (Kuo, 2001,

Bhullar, 2007).

3. RESULTS AND DISCUSSION

The synthetic and analytical data of the C60/PvPy conjugates were synthesized under different supercritical conditions have been summarized (Table 1) and the synthetic data revealed that AIBN initiated polymerization of VPy in presence of C60 has been greatly influenced by supercritical conditions and concentration of AIBN and VPy respectively (Table I). This has in turn affected the recovery of C60 and rheoviscosity of the corresponding PvPy-C60 derivatives. By increasing the VPy concentration ranging $6.95\text{--}20.85 \times 10^{-3}$ mol/dL, corresponding yield of product in decreasing order was 48.79–28.0, probably due to the lack of required concentration of initiator. By increasing the concentration of initiator ranging $304.5\text{--}1218.0 \times 10^{-3}$ mol/dL, product yield was gradually increased ranging 10.3–48.8 % with highest at AIBN concentration: 609.0×10^{-3} mol/dL. Increasing the pressure and time have caused decreasing effect over the yield of the product, whereas increasing the temperature has significantly contributed to yield of the product. These observations clearly indicate that AIBN initiated polymerization of VPy in presence of C60 has afforded the corresponding PvPy-C60 conjugates at increasing yield with increase in AIBN concentration.

The polymerization progress of VPy in presence of C60 under different supercritical conditions has shown regular variations in the rheoviscosity of the resulting C60/PvPy conjugates with increase in AIBN concentration and temperature with increase in concentration of AIBN ranging $304.5\text{--}1218 \times 10^{-3}$ mol/dL a regular increase in rheoviscosity ranging 0.32–0.86 Mpa sec of corresponding conjugates was observed. This data clearly indicates that polymerization of VPy in presence of C60 was induced toward higher molecular mass gain with increase in AIBN concentration. Polymerization of VPy in presence of C60 was greatly enhanced with temperature ranging 60–90 °C. This has shown corresponding rheoviscosity ranging 0.32–1.13 Mpa sec. Increasing the time has contributed an irregular variation in the rheoviscosity of the corresponding

C60/PvPy conjugates.

By increasing the PvPy concentration ranging 6.95–20.84 mol./dL the corresponding C60/PvPy conjugates have shown rheoviscosity ranging 1.16–0.98 Mpa sec. Effect of the pressure on polymerization of VPy was investigated in the range of 1200–1800 psi. This has contributed a decrease 0.37 MPA sec. in the rheoviscosity of the conjugates ranging 1.16–0.37. Such decrease in rheoviscosity of the C60/PvPy conjugates may be due to the incomplete polymerization of the monomer under the investigated conditions (Gumbos, 2005, Bhullar, 2007).

Uv-vis spectra of VPy, PvPy and corresponding PvPyC60 conjugates were recorded in methanol. Due to least solubility in methanol, Uv-vis spectra of C60 were recorded in toluene [Figure 1]. VPy shows absorption at 295 nm that was shifted to 289 nm corresponding to PvPy synthesized under identical conditions as applied for corresponding PvPy/C60 conjugate. The later has shown absorption at 286 nm in methanol. These observations indicate that an appropriate mixing of the wave function of C60 with PVPy, that may cause the formation of star structure (Kuo, 2001, Gabriela, 2005, Wang, 2004). Effect of C60 content on the morphology of corresponding C60/PvPy conjugates was evaluated through their comparative SEM. The PvPy has shown heterogeneous morphology [Figure 2(a)] polymerization of VPy in the presence of C60 has rendered corresponding C60/PvPy conjugate with appearance of clear domains of C60 [Figure 2(a-b)]..(Cooper, 2000 Chen, 2000)..

4. CONCLUSION

Polyvinyl pyridine (PvPy) /C60 conjugates were synthesized through 2, 2-azobisisobutyronitrile initiated insitu polymerization of PvPy under a series of reaction conditions in scCO_2 . Polymerization of VPy in C60 was progressed by increasing the rheoviscosity with concentration of AIBN and temperature under applied supercritical conditions. Presence of C60 into PvPy was ascertained through Uv-vis, spectra and scanning electron microscopy. Uv-vis spectra indicate the formation of C60/PvPy as star structure.

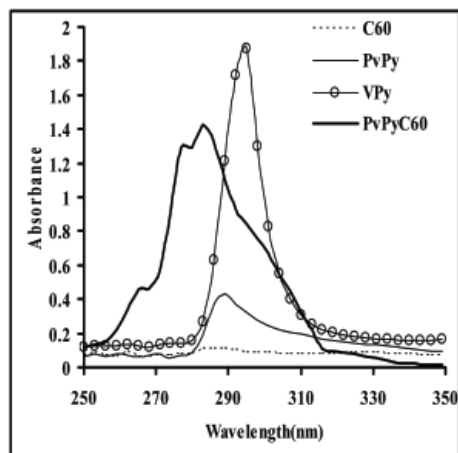


Figure 1: Uv-vis spectra

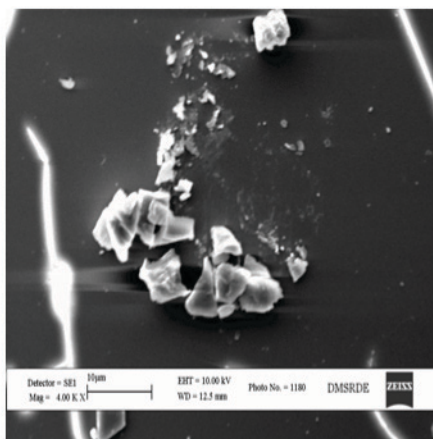


Figure 2(a): PvPy

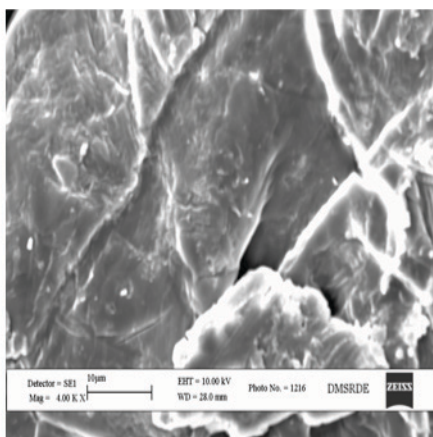


Figure 2(b): C60/PvPy (49.9%)

Table1: Synthesis and rheoviscometric data of C60/PvPy Conjugates

S.NO.	Reaction Variables	Variations	Yield (%)	Rh.Visco. (MPa sec)	Experimental condition
1	VPy ($\times 10^{-3}$) mole/dL	6.95	48.79	1.16	80 \pm 1 °C, 1200 psi,
		13.90	41.80	0.98	[AIBN] 609.0 $\times 10^{-3}$
		17.37	31.80	0.77	mole/dL, 4hrs, [C60]
		20.85	28.0	0.58	: 100 \pm 1 mg
2.	AIBN ($\times 10^{-3}$) mole/dL	304.5	10.3	0.32	80 \pm 1 °C, 1200 psi,
		609.0	48.8	1.14	[VPy] 6.95 $\times 10^{-3}$
		913.5	37.0	0.91	mole/dL, 4hrs, [C60]
		1218.0	36.0	0.86	: 100 \pm 1 mg
3	Pressure (psi)	1200	48.79	1.16	80 \pm 1 °C, [VPy] 6.95
		1400	39.0	0.92	$\times 10^{-3}$ AIBN] 609.0
		1600	23.1	0.42	$\times 10^{-3}$ mole/dL, 4hrs,
		1800	22.0	0.37	[C60]: 100 \pm 1 mg
4.	T (°C)	60	21.6	0.32	1200psi,
		70	49.9	1.24	[VPy] 6.95 $\times 10^{-3}$
		80	48.79	1.14	[AIBN] 609.0
		90	47.6	1.13	$\times 10^{-3}$ mole/dL, 4hrs, [C60]: 100 \pm 1 mg
5	Time(hrs)	3.0	39.0	0.92	80 \pm 1 °C, [VPy] 6.95
		4.0	48.79	1.16	$\times 10^{-3}$ [AIBN] 609
		5.0	31.8	0.77	$\times 10^{-3}$ mole/dL, 1200
		6.0	30.7	0.65	psi [C60]: 100 \pm 1 mg

ACKNOWLEDGEMENTS

Financial support from the project grant No. ERIP/ER/ 0403449/ M/ 01 funded by Government of India is acknowledged.

References

1. Chen, Y.; Huang, Z.; Kong, R. C. S.; Chen, S.; Shao, Q.; Yan, X.; Zhao, F.; Fu, D. 2000 Synthesis and characterization of soluble C60-chemically modified poly(p-bromostyrene) *China Journal of Polymer Science Part A: Polymer Chemistry*. 34(16), 3297 – 3302..
2. Cooper, A.I.; Wood, C D.; Holmes, A B. 2000. Synthesis of well-defined macroporous polymer monoliths by sol-gel polymerization in supercritical CO₂. *Ind. Eng. Chem. Res* 39.4741-4744.
3. Ford, W. T.; Lary, A. 1999., Fullerene-containing polymers. *Polymer Data Handbook*. Oxford University Press, Inc. 118-120,
4. Gabriela, A. ; Gabrielle, C.C. ; Jacques, D. ; Michel, N.J. ; Bogdan, C. S. ; Jack, C. 2005. Multifunctional, water-soluble, C60-pendant maleic anhydride copolymer, *J. Polym . Sci Part A: Polym. Chem.* 43, 5814-5822.
5. Geckeler, K.E.; Samal, S. 2004. Syntheses and properties of macromolecular fullerenes, a review *Russian Journal of Applied Chemistry*. 78 (1), 130-136.
6. Gombos, Z.; Nagy, Mihályvas, V. L.; Gaál .J. 2005. Investigation of pore size and resin absorbency in chopped strand. mats, *Periodical Polytechnica Ser. Mech. Eng.* 49(2), 131–148.
6. Kuo, C. Kumar, J. Tripathy, S. K.; Long, Y.; Chiang, J. 2001. Synthesis and properties of [60] fullerene-polyvinyl pyridine conjugates for photovoltaic devices *Macromol. Sci. Pure Appl. Chem.* A38 (12), 1481–1498.
7. Mountrichas, G.; Pispas, S.; Kamitsos, E. I.; Xenogiannopoulou, E.; Couris, S. 2005. Stable aqueous dispersions of C60 fullerene by the use of a block copolymer *Journal of Physics: Conference Series* .10 .163–166.
8. S. Shi, K.C. Khemanikc , Q.C. Li, F. Wud l, A. J Am Chem Soc., 114(26), (1992)10656..
9. Sun, Y.P.; Liu, B.; Morton, D.K. 1996. Preparation and characterization of a highly water-soluble pendant fullerene polymer. *Chem. Commun.* (24):2699–700.
10. Wang, C.; Guo, Z.; Fu, S.; Wu, W.; Zhu, D. 2004 Polymers containing fullerene or carbon nanotube structures. *Prog. Polym. Sci.* 29 1079–1141.
11. Zaidi, M.G.H.; Bhullar, N.; Singh, V.P.; Sah, P.L.; Alam, S.; Singh, R. 2006 Mechanical and thermal properties of epoxy polymethyl methacrylate blends synthesized in supercritical carbon dioxide. *J. Appl. Polym Sci.* Vol.103 (2), 1303-1310.