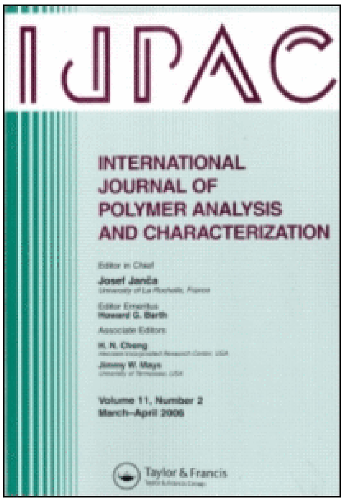

International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

^{13}C NMR and Raman Studies of Fullerene-Based Poly(Methyl Methacrylate) Polymers

Supriya Porwal[a]; Ashutosh Dwivedi[a]; Meet Kamal[b]
[a] Department of Physics, Maharana Pratap Engineering College, Kanpur, India [b] Department of Chemistry, Christ Church College, Kanpur, India

To cite this Article Porwal, Supriya , Dwivedi, Ashutosh and Kamal, Meet(2009) '^{13}C NMR and Raman Studies of Fullerene-Based Poly(Methyl Methacrylate) Polymers', International Journal of Polymer Analysis and Characterization, 14: 6, 551 — 562

To link to this Article: DOI: 10.1080/10236660903086185

URL: http://dx.doi.org/10.1080/10236660903086185

International Journal of Polymer Anal. Charact., 14: 551–562, 2009
Copyright © Taylor & Francis Group, LLC
ISSN 1023-666X print
DOI: 10.1080/10236660903086185

Taylor & Francis
Taylor & Francis Group

^{13}C NMR and Raman Studies of Fullerene-Based Poly(Methyl Methacrylate) Polymers

Supriya Porwal,[1] Ashutosh Dwivedi,[1] and Meet Kamal[2]
[1]Department of Physics, Maharana Pratap Engineering College, Kanpur, India
[2]Department of Chemistry, Christ Church College, Kanpur, India

Abstract: ^{13}C NMR and Raman studies of a series of polymeric samples of fullerene-grafted poly(methyl methacrylate), which were prepared by systematic variation of concentration of fullerene and methyl methacrylate, are described. ^{13}C NMR spectral analysis of the polymeric samples showed a peak for fullerene at 138 δppm and for poly(methyl methacrylate) between 169 and 177 δppm, and Raman spectral analysis of the polymeric samples gave the Raman shift for fullerene between 1400 and 1600 cm^{-1} and poly(methyl methacrylate) at 2800 cm^{-1}. The T_g value, obtained from DSC results, showed a high glass transition temperature at 305.7°C, revealing the presence of fullerene in the polymeric matrix.

Keywords: Coupling constant; Fullerene; Glass transition temperature; Methyl methacrylate; ^{13}C NMR; Raman spectroscopy

Submitted 21 April 2009; accepted 3 June 2009.

The authors are grateful to the Director, Maharana Pratap Engineering College, and late Prof. A. K. Srivastava, Harcourt Butler Technological Institute, Kanpur, for providing necessary facilities and help when needed. We are also grateful to Advanced Centre of Material Sciences, IIT Kanpur, for providing Raman and NMR facilities.

Correspondence: Ashutosh Dwivedi, Department of Physics, Maharana Pratap Engineering College, Kanpur, India. E-mail: ashu_dwi@yahoo.com

INTRODUCTION

A polymer is a material whose molecules contain a very large number of atoms linked by covalent bonds that make them macromolecules. The field of synthetic polymers or plastics is currently one of the fastest growing material industries. In addition to these synthetic materials, different types of carbon materials called fullerenes have recently been introduced.[1] Fullerene, in its most stable form C_{60}, exhibits a variety of outstanding electronic, conducting, and magnetic properties[2] and acts as photo sensitizer and photorefractive material.[3] The science of fullerenes continues to be an exciting field, generating many articles with promising new applications every year. A search of the literature reveals that a lot of work has been carried out on synthesis, characterization of fullerenes, and doped fullerenes with alkali metals like potassium and rubidium ternary compounds,[4,5] poly fulleride ions in AC_{60}[6] (A is potassium, rubidium, or cesium), and fullerene doped with organic cations like morpholine and acridizine.[7] The literature survey also reveals that ^{13}C NMR spectroscopic studies of fullerene and polyethylene oxide complexes,[8] magnetic resonance of solid fullerene and their compounds with alkali metals,[9] and superconductivity and nuclear magnetic resonance investigation of $KTl_{1.5}$-doped C_{60}[10] have been carried out in past years. Synthesis and cationic photopolymerization of a C_{60} derivative bearing a 2,4,6-tris(epoxynonyloxy)phenyl moiety (FB9ox)[11] has been carried out. In addition, the synthesis and determination of properties of poly (methyl methacrylate)/clay nanocomposites, prepared via in situ polymerization with nickel acetyl acetonate [Ni(acac)$_2$] catalyst in combination with methylalumoxane,[12] have also been carried out. The literature also reveals Raman spectroscopic studies on pressure-induced polymerization of C_{60} at high temperature,[13] rotation vibrational dynamics of C_{60},[14] and the vibrational Raman spectra of C_{60}.[15] High-temperature study of solid C_{60},

Table I. Variation of fullerene with poly(methyl methacrylate)

Sample name	Fullerene (mol/L)	Poly(methyl methacrylate) (mol/L)
A	1.77×10^{-5}	4.19
B	1.38×10^{-4}	3.77
C	1.89×10^{-4}	3.42
D	2.31×10^{-4}	3.14
E	1.26×10^{-4}	4.27
F	1.73×10^{-4}	2.35

Table II. ^{13}C NMR of plain fullerene and fullerene-based poly(methyl methacrylate)

Sample name	C_{60} (δppm)	Poly (methyl methacrylate) (δppm)	Equatorial position of C-atoms	$CDCl_3$ (δppm)	$\alpha-CH_3$ (δppm)	OCH_3 (δppm)	Cα Poly (methyl methacrylate) (δppm)
Plain fullerene	138	–	129, 128	77, 77.2, 77.5	21.6	–	–
A	136	169.2, 169.4, 169.6, 169.8	–	77	21.0	51	–
B	143	169	127, 129	76.8, 77.1, 77.3	21.6	53	45
C	134	177.0, 177.9, 178.2	128, 129	76.8, 77.1	18.8	51	44.6, 44.9
D	139	170	128, 129	76.8, 77.1	19	61	–
E	138	178	128, 129	76, 77	21.3	–	40.2, 40.3
F	138	172	128, 129	76, 77	27.1	62.01	–

pristine and polymerized, was performed by Raman spectroscopy up to 843 K.[16] These data could be used as a reference for in situ studies of C_{60} chemical transformation occurring at high temperature. Selective multi-addition of organocopper reagents to fullerenes[17] were also carried out. To achieve selective multi-addition of organometallic reagents to fullerenes, one needs to control not only the number of organic groups to be added but also the regioselectivity of the addition, and the yield on each step must be very high to achieve high overall yield of the multiple reaction. The literature survey shows sufficient study on radical polymerization of vinyl monomers in the form of homopolymer, copolymer, and terpolymer.[18–20] However, spectroscopic studies on fullerene-grafted vinyl monomers are still scarce. The present article therefore highlights ^{13}C NMR and Raman spectroscopic studies of fullerene-grafted poly(methyl methacrylate) polymers.

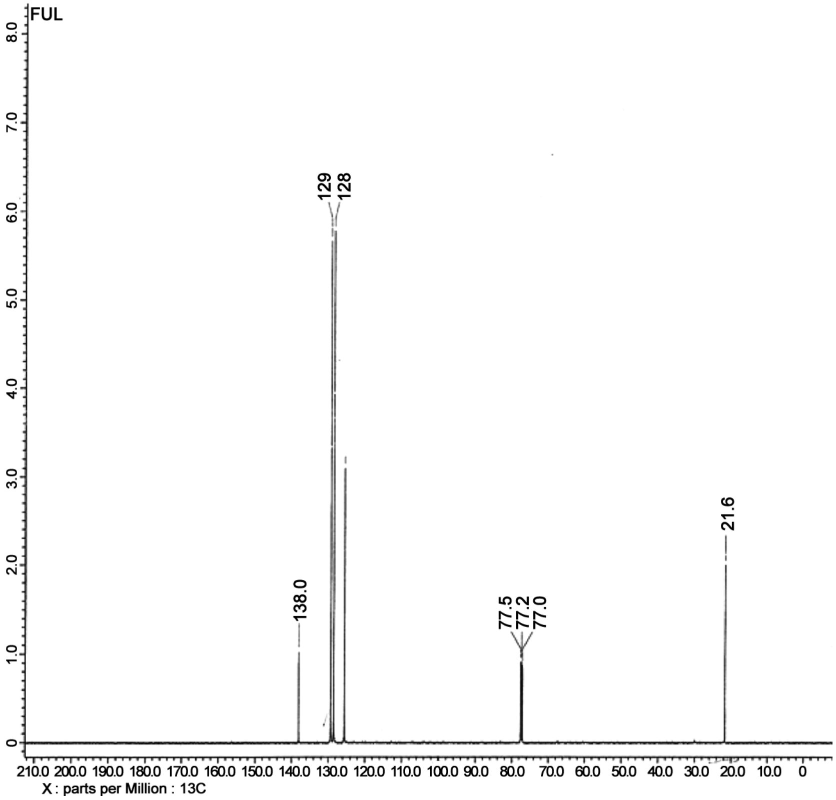

Figure 1. ^{13}C NMR of plain fullerene.

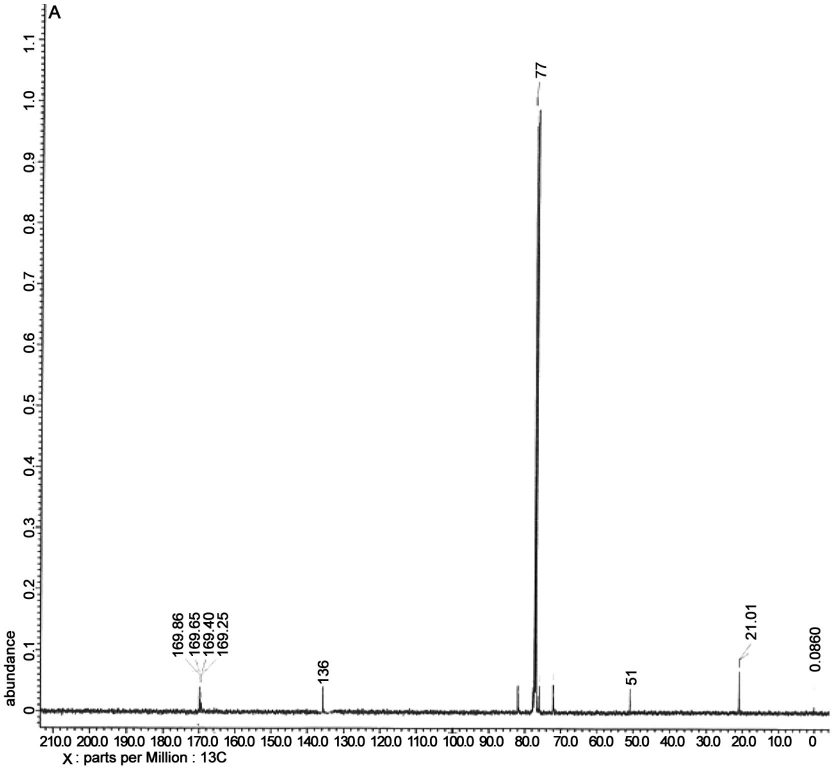

Figure 2. ^{13}C NMR of sample A.

EXPERIMENTAL SECTION

Purified solvents were used as received. Benzoylperoxide (BPO) was recrystallized in chloroform. Fullerene (Alfa Aesar, 99.9% C_{60}) was used as received and was dissolved in toluene as required. A series of samples (A to F) of fullerene-grafted poly(methyl methacrylate) were synthesized by systematic variation of fullerene (1.77×10^{-5}–1.73×10^{-4} mol/L) and methyl methacrylate (4.19–2.35 mol/L) concentration using benzoylperoxide as initiator and toluene as solvent for 1 h at 90°C under nitrogen. The polymer was precipitated in acidified methanol and vaccum dried until a constant weight was obtained. The fullerene concentration versus methyl methacrylate concentration for each synthesized sample is depicted in Table I.

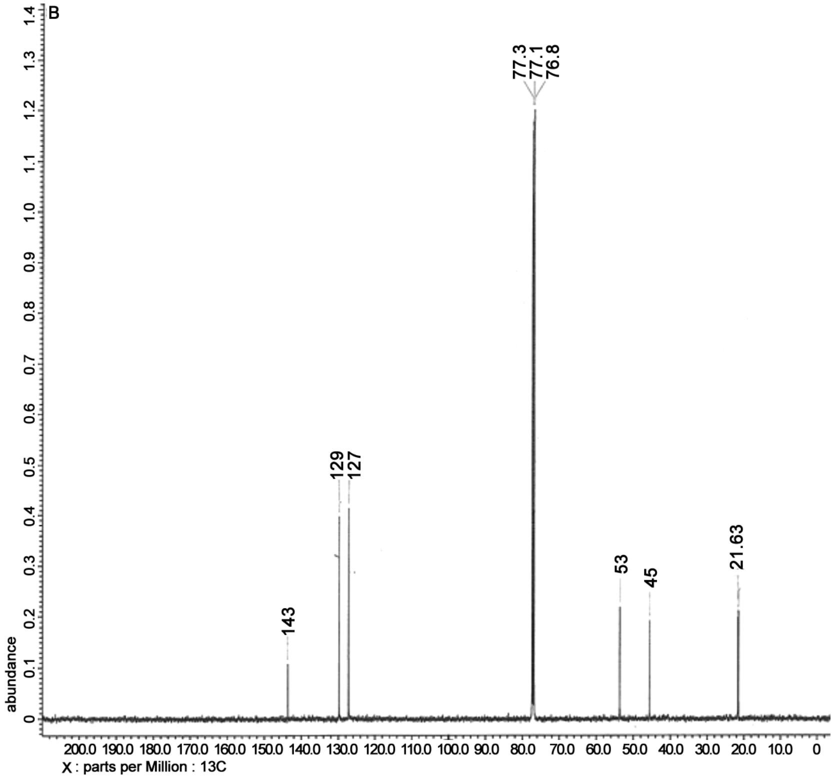

Figure 3. ^{13}C NMR of sample B.

CHARACTERIZATION OF POLYMERS

Spectral Analysis: ^{13}C NMR Spectroscopy

^{13}C nuclear magnetic resonance (NMR) spectral analysis of plain fullerene and fullerene-grafted poly(methyl methacrylate) samples (A to F) (Table II) was carried in an ECX 500-JEOL NMR spectrometer using $CDCl_3$ as a solvent. The peak values were studied and the coupling constant (τ) was determined.

Raman Spectroscopic Studies

Raman spectra of fullerene-based poly(methyl methacrylate) were recorded by NSOM (near-field scanning optical microscope), laser 514.7 nm.

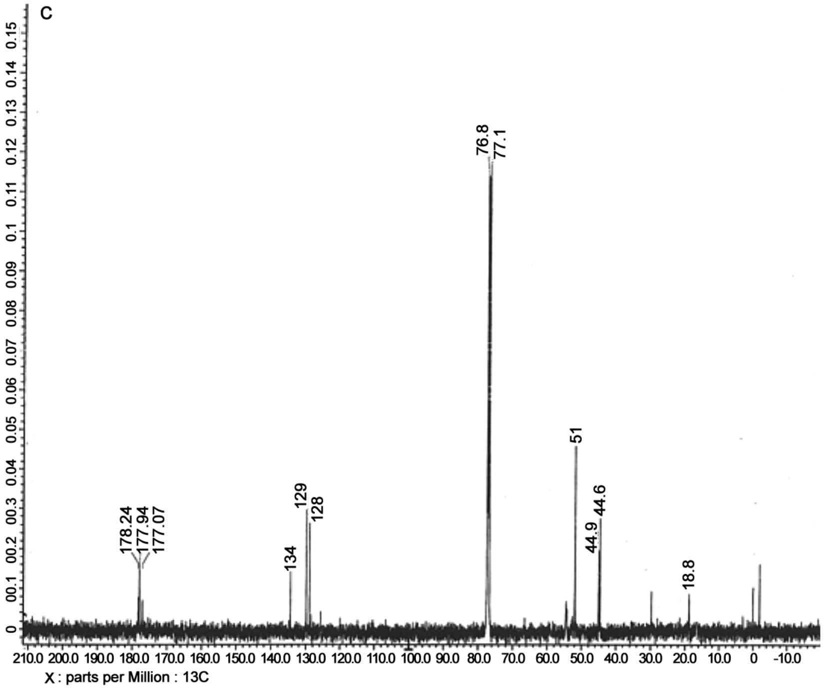

Figure 4. ^{13}C NMR of sample C.

Thermal Properties

Differential scanning calorimetry was carried out on a V2.2 Dupont calorimeter, under nitrogen atmosphere at a heating rate of 10°C/min. The sample weight was 3–5 mg.

RESULTS AND DISCUSSION

^{13}C NMR spectrum for C_{60} shows a peak at 138 δppm, which is due to proton decoupling. Peak values corresponding to $CDCl_3$ were obtained between 77.0 and 77.5 δppm, equatorial position of carbon atoms was at 129 δppm, and α-CH_3 at 21.6 δppm (Figure 1). Further polymeric samples (A to F) were obtained by systematic variation of fullerene and poly (methyl methacrylate). These samples were studied by ^{13}C NMR spectroscopy, whose spectra are given in Figures 2–7 and whose comparison is given in Table II. From the observed data, we find that there is a shift in peak values of methyl methacrylate (MMA) and plain fullerene, thereby showing incorporation of the polymer formed on the

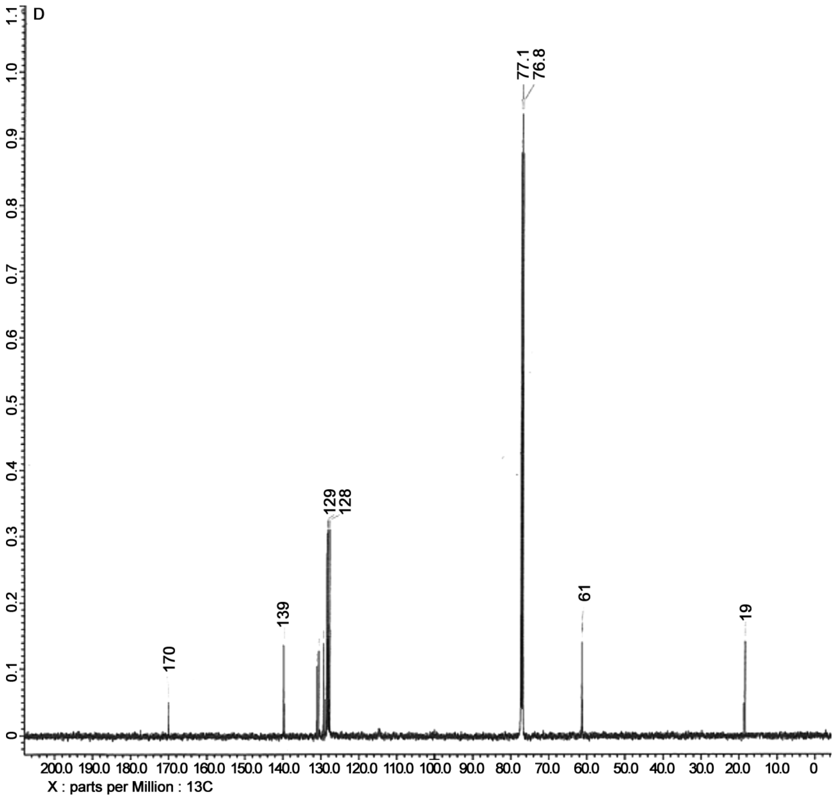

Figure 5. ^{13}C NMR of sample D.

fullerene surface, which increases the solubility and processability of the polymer network.

Raman spectroscopy yields important information about the structure of macromolecules. We are able to determine the orientation and conformation of polymers and the density of vibrational states by using this technique. A strong band of fullerene and poly MMA interaction is manifested as the pronounced shift of fullerene at 1500 cm^{-1}, which is usually obtained at about 1466–1470 cm^{-1}, and that of the peaks at about 1420–1430 cm^{-1}, which are the H_g modes (Figure 8). A strong band between 2900 and 3000 cm^{-1} shows the presence of –CH stretching groups. There is no band at 1900–2400 cm^{-1}, which indicates that the double bond of MMA is not present, i.e., MMA has been polymerized. Also, a band at 1725 cm^{-1} shows the presence of carbonyl group of poly MMA. Differential scanning calorimetry (DSC) result shows a glass transition temperature (T_g) at 305°C of the polymeric sample (Figure 9),

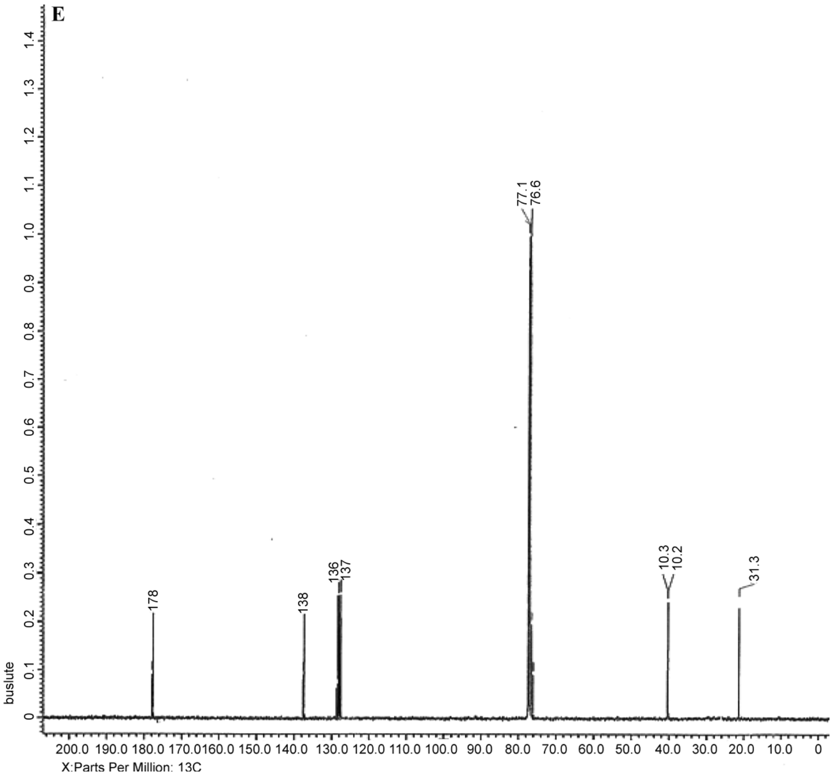

Figure 6. ^{13}C NMR of sample E.

whereas the T_g value reported for poly MMA is 130°–140°C[25] and that of fullerene is between 200° and 250°C. The high value of T_g shows that the poly MMA has been incorporated on the C_{60} framework.

CONCLUSION

To summarize, we have given a detailed ^{13}C NMR investigation of fullerene-grafted poly(methyl methacrylate) showing peak values between 134 and 143 δppm, as compared to ^{13}C NMR spectrum studies of plain fullerene at 138 δppm, which was agreement with the results reported earlier. A band of fullerene and poly(methyl methacrylate) interaction is observed at 1500 cm^{-1}, which is usually obtained at about 1466–1470 cm^{-1}. Also, the high value of T_g obtained at 305°C shows the interaction of poly(methyl methacrylate) chains on the fullerene surface.

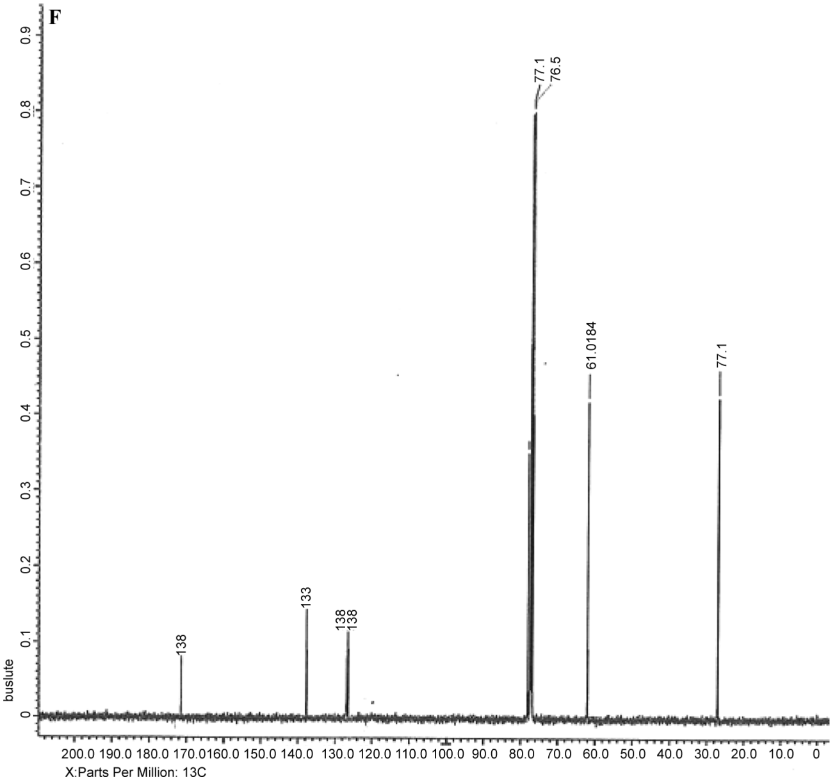

Figure 7. ^{13}C NMR of sample F.

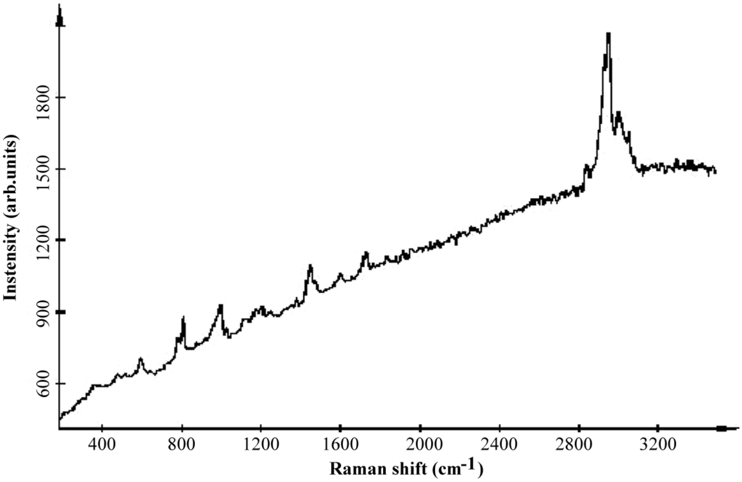

Figure 8. Raman spectra of sample F.

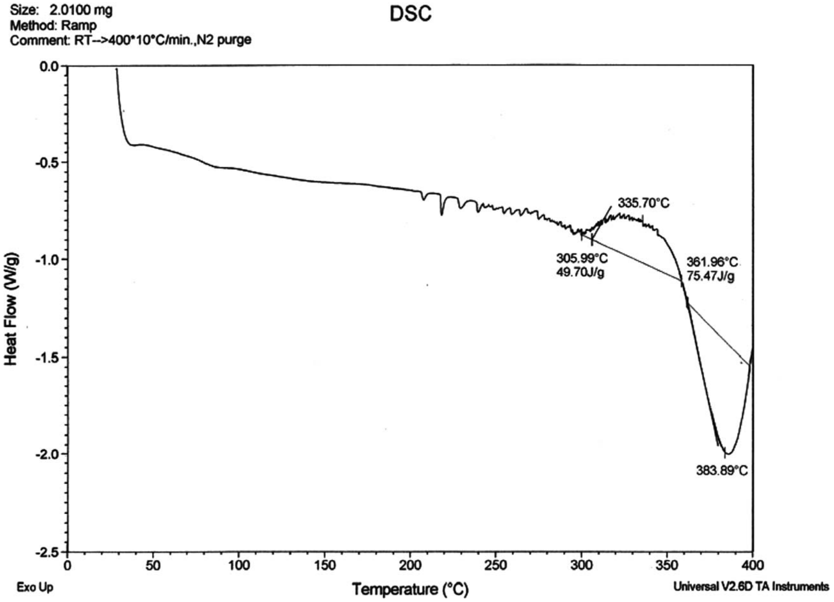

Figure 9. DSC curve of sample E.

REFERENCES

[1] Kroto, H. (1992). Introduction [to Special Issue on Fullerenes]. *Carbon* **30** (8), 1139–1141.

[2] Zheng, L. A., E. V. Barrera, and R. D. Shull. (2002). Formation and stabilization of nanosize grains in ferromagnetic thin films by dispersed C_{60}. *J. Appl. Phys.* **92**, 523.

[3] Martin-Gomis, L., J. Ortiz, F. Fernández-Lazaro, A. Sastre-Santos, B. Elliot, and L. Echegoyen. (2006). Synthesis and characterization of new trinitroflourene-fullerene dyads as photosensitizers in photorefractive polymer materials. Redox behavior and charge transfer properties. *Tetrahedron* **62** (9), 2102–2109.

[4] Alloul, H., K. Holczer, Y. Yoshinari, and O. Klein. (1994). ^{39}K NMR study of phase transitions and electronic properties in K_3C_{60}. *Physica C* **235**, 2509–2510.

[5] Alloul, H., K. Halczer, Y. Yoshinari, and L. Forro. (1994). NMR study of RbC_{60}. *Physica C* **235**, 2479–2480.

[6] Pekker, S., G. Oszlanyi, and G. Faigel. (1998). Structure and stability of covalently bonded polyfulleride ions in A_xC_{60} salts. *Chem. Phys. Lett.* **282**, 435–441.

[7] Zuzok, R., P. Wzietek, M. Fourmigue, P. Batail, P. Auban-Senzier, S. Roth, and D. Jerome. (1993). C_{60} doped with organic cations: Magnetic resonance measurements. *Synth. Met.* **56** (2–3), 3235–3239.

[8] Li, M., and Q. Chen. (2003). Interactions between fullerene (C_{60}) and poly(ethylene oxide) in their complexes as revealed by high-resolution solid-state ^{13}C NMR spectroscopy. *Polymer* **44** (9), 2793–2798.

[9] Mizoguchi, K. (1993). Magnetic resonance of fullerene solids and their compounds. *J. Phys. Chem. Solids* **54** (12), 1693–1698.

[10] Krous, M., J. Freyteg, S. Gartner, H. M. Vieth, W. Kratschmer, and K. Luders. (1991). Superconductivity and NMR investigations of $KTI_{1.5}$-doped C_{60}. *Z. Phys. B Condens. Matter* **85**, 1.

[11] Lintinen, K., A. Efimov, S. Hietala, S. Nagao, P. Jalkanen, N. Tkachenko, and H. Lemmetyinen. (2008). Cationic photopolymerization of liquid fullerene derivative under visible light. *Polym. Sci. Part A Polym. Chem.* **46** (15), 5194.

[12] Cui, L., N. H. Tarte, and S. I. Woo. (2008). Synthesis and properties of poly(methyl methacrylate)/clay nanocomposites prepared via in situ polymerization with $Ni(acac)_2$ catalyst. *J. Appl. Polym. Sci.* **110** (2), 784–790.

[13] Talyzin, A. V., L. S. Dubrovinsky, T. Le Bihan, and U. Jansson. (2002). Pressure-induced polymerization of C_{60} at high temperatures: An in situ Raman study. *Phys. Rev. B* **65**, 245413.

[14] Rajailov, P. M., V. G. Hadjiev, A. R. Goni, and C. Thomsen. (1999). Rotation-vibrational dynamics of solid C_{60}: A Raman study. *Phys. Rev. B* **60**, 13351.

[15] Dennis, T. J., J. P. Hare, H. W. Kroto, R. Taylor, D. R. M. Walton, and P. J. Hendra. (1991). The vibrational Raman spectra of C_{60} and C_{70}. *Spectrochim. Acta* **47**, 1289–1292.

[16] Talyzin, A. V., A. Dzwilewski, and T. Wagberg. (2006). Temperature dependence of C_{60} Raman spectra up to 840 K. *Solid State Commun.* **140**, 178–181.

[17] Matsuo, Y., and E. Nakamura. (2008). Selective multiaddition of organocopper reagents to fullerenes. *Chem. Rev.* **108** (8), 3016–3028.

[18] Liu, Y.-L., M.-C. Tseng, and M.-H. Fangchiang. (2008). Polymerization and nanocomposites properties of multifunctional methylmethacrylate POSS. *J. Polym. Sci. Part A Polym. Chem.* **46** (15), 5157–5166.

[19] Agarwal, B. P., and A. K. Srivastava. (1994). Radical terpolymerization by zinc acrylate, acrylonitrile and styrene initiated by styrene arsenic sulfide complex. *Polym. Eng. Sci.* **34** (6), 528–531.

[20] Bhatnagar, U., and A. K. Srivastava. (1992). Metal-ylide complex initiated radical copolymerization of methylmethacrylate and styrene. *J. Macromol. Sci. Pure Appl. Chem.* **A29** (4–5), 357–370.