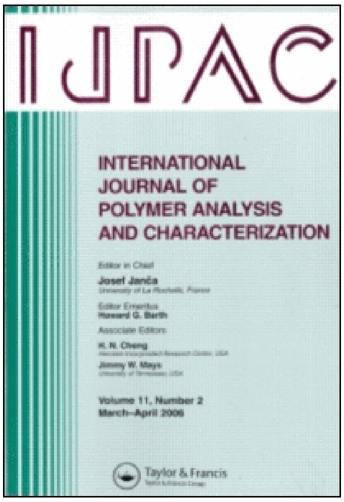


International Journal of Polymer Analysis and Characterization
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713646643

Synthesis and Properties of [60] Fullerene-Polymethyl Methacrylate Conjugates in Supercritical Carbon Dioxide

V. Agrawal[a]; S. Vishnoi[a]; M. G. H. Zaidi[a]; S. Alam[b]; A. K. Rai[c]
[a] Supercritical Fluid Processing Laboratory, Department of Chemistry, G. B. Pant University of Agriculture and Technology, Pantnagar, India [b] Defense Materials Stores Research Development and Establishment, Kanpur, India [c] Department of Physics, Allahabad University, Allahabad, India

To cite this Article Agrawal, V. , Vishnoi, S. , Zaidi, M. G. H. , Alam, S. and Rai, A. K.(2010) 'Synthesis and Properties of [60] Fullerene-Polymethyl Methacrylate Conjugates in Supercritical Carbon Dioxide', International Journal of Polymer Analysis and Characterization, 15: 5, 267 — 276

To link to this Article: DOI: 10.1080/10236661003758913

URL: http://dx.doi.org/10.1080/10236661003758913

International Journal of Polymer Anal. Charact., 15: 267–276, 2010
Copyright © Taylor & Francis Group, LLC
ISSN: 1023-666X print
DOI: 10.1080/10236661003758913

Taylor & Francis
Taylor & Francis Group

SYNTHESIS AND PROPERTIES OF [60] FULLERENE-POLYMETHYL METHACRYLATE CONJUGATES IN SUPERCRITICAL CARBON DIOXIDE

**V. Agrawal,[1] S. Vishnoi,[1] M. G. H. Zaidi,[1]
S. Alam,[2] and A. K. Rai[3]**
[1]*Supercritical Fluid Processing Laboratory, Department of Chemistry, G. B. Pant University of Agriculture and Technology, Pantnagar, India*
[2]*Defense Materials Stores Research Development and Establishment, Kanpur, India*
[3]*Department of Physics, Allahabad University, Allahabad, India*

[60] Fullerene (C60) almost completely inhibits the polymerization of most vinyl monomers, but our investigation shows that the concentration of radical initiators and reaction conditions greatly enhances conjugation formation. In the present investigation, a series of [60] fullerene-polymethyl methacrylate conjugates was synthesized through 2,2-azobisisobutyronitrile (AIBN)-initiated in situ polymerization of methyl methacrylate (MMA) under different reaction conditions in supercritical carbon dioxide (scCO$_2$). This has afforded corresponding [60] fullerene-PMMA conjugates with [60] fullerene content (%) and rheoviscosity range of 0.79–4.69% and 1.069–1.345 Mpa s, respectively. The process of in situ polymerization was monitored at different concentrations (molldL) of AIBN ($304.50–761.25 \times 10^{-3}$) and MMA ($9.41–23.53 \times 10^{-3}$), and temperatures (60°–90°C), pressures (1400–2000 psi), and time (2–8 h). The progress of in situ polymerization was monitored rheoviscometrically in tetrahydrofuran at 25 ± 1°C. Selected [60] fullerene-PMMA conjugates were characterized through UV-vis, GPC, FT-IR, ^{1}HMMR, ^{13}CNMR spectra, and thermal characterization by TG.

Keywords: [60] Fullerene; Polymethyl methacrylate; Supercritical carbon dioxide

INTRODUCTION

The conventional methods for synthesis of [60] fullerene-polymers not only involve toxic, flammable, and costly solvents as a reaction medium but also pose a problem in separation and isolation of the products from the reaction medium.[1] Over the past few decades, supercritical fluids, including supercritical carbon dioxide (scCO$_2$), have gained significant technological uses due to their gas-like diffusivity

Submitted 10 February 2010; revised 4 March 2010; accepted 9 March 2010.
Financial support from the Project Grant No. ERIP/ER/0403449/M/01 funded by the Government of India is acknowledged.

Correspondence: V. Agrawal, Supercritical Fluid Processing Laboratory, Department of Chemistry, G. B. Pant University of Agriculture and Technology, Pantnagar, Uttarakhand-263 145, India. E-mail: hi_vikashagrawal@rediffmail.com

and liquid-like density.[2,3] The unique diffusion property of $scCO_2$ increases the free volume and mobility of the polymer chains with simultaneous reductions in the glass transition temperature and viscosity. Very few efforts have been reported to synthesize fullerene or carbon nanotube conjugated polymers in $scCO_2$.[4,5]

In the past few years a number of efforts have been made to synthesize fullerenated vinyl polymers by reacting various monomers, e.g., polystyrene sulfonate,[6] 4-vinylpyridin,[6,7] vinylbenzylchloride,[8] N-vinylcarbazole,[9] and vinylpyrrolidone.[10]

AIBN-initiated radical polymerization of 2-cyanoethyl acrylate and cyanovinyl acetate in the presence of [60] fullerene (C60) produces copolymers in good yields,[11] but on the other hand, C60 almost completely inhibits the polymerization.[10,11] Wang et al.[4] reported, for the first time, polymerization in which $scCO_2$ is used simultaneously as both an antisolvent and a polymerization medium to create C60-polymer composite microparticles.[12] Recently, Camp et al.[11] have reported the copolymerization of C60 and styrene in the presence of a large excess of the initiator AIBN. According to the authors, the radicals from the initiator undergo multiple additions on C60, ultimately changing its nature sufficiently such that it would not inhibit polymerization.

In past few years a number of efforts have been made to polymerize MMA in $scCO_2$,[4,13] and it was also polymerized in the presence of C60,[11,14] but no effort has been reported to synthesize fullerene conjugate PMMA in $scCO_2$.

In this research, we investigate a "green" process for the continuous polymerization of methyl methacrylate in the presence of C60 by free-radical precipitation polymerization in $scCO_2$. The objective of this study was to determine how general is the inhibition of radical polymerization by C60 and to determine the role of different reaction conditions in the polymerization.

EXPERIMENTAL SECTION

Starting Materials

The monomer methyl methacrylate (MMA) was purchased from Acros Chemicals USA. C60 ($\geq$99.5%) was purchased from SES Research (USA). 2,2-Azobisisobutyronitrile (AIBN) was purchased from Himedia Laboratories (India) and was used without further purification. Solvents for UV-vis spectroscopy were purchased from Spectrochem (India). Other chemicals used were of AR grade. Carbon dioxide (99.9%), used as supercritical solvent, was locally purchased.

Synthesis of [60] Fullerene-Containing Polymers in $scCO_2$

All [60] fullerene-PMMA conjugates were synthesized in a stainless steel high-pressure reactor (100 cm^3), model MC 10 10 SI ST equipped with PID temperature controller, manufactured by Pressure Products Industries (USA).[15] The reactor was charged with required quantities of C60, monomer, and AIBN. The cell was initially pressurized with carbon dioxide (99.99%) and then gradually heated with an electrical heating tape wrapped around the exterior of the cell in the temperature range $50–90 \pm 1°C$ to obtain the desired pressure. The temperature inside the cell was measured by an industrial insulated thermocouple provided and displayed on the

PID temperature controller. The reaction mixture was refluxed in $scCO_2$ over 2 to 26 h. The cell was cooled to 25 ± 1°C and the CO_2 was vented into dichloromethane. The cell was opened to give C60-PMMA conjugates (Table I).

Characterization

The rheoviscometry measurements were carried out 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 it took the ball to sink 30 mm deep in the cuvette was measured.[16] UV-vis spectra were recorded using a model Genesis 10 spectrophotometer (Thermospectronic, USA).[17] The molecular weights were recorded by a Varian Pro Star GPC with 355 RI detector by using tetrahydrofurane (THF) as a mobile phase at 270 psi pressure with a flow rate of 1 mL/min, injection time of 10 min, and room temperature 37°C. Fourier transform-infrared (FT-IR) spectra were recorded on a Brucker FT-IR Spectrophotometer in KBr.[18] ^1H nuclear magnetic resonance (NMR) spectra were recorded on a Brucker Av400. $CDCl_3$ was used as a solvent. ^{13}C NMR spectra were also recorded on the Brucker Av400 and C_6D_6 was used as a solvent. Simultaneous differential thermogravimetric analysis (TG) was performed by using a Netzsch-Geratebau thermal analyzer model STA-409 in static air at 25°C/10 (K/min)/1000°C.[19]

Table I. Synthesis of C60-PMMA conjugates under different reaction conditions in $scCO_2$

Sample no.	Variables	Variations	Yield (%)	C60 (%)	Rheoviscosity (MPa s)	Mw (g/mol)	P.D.
1	MMA[a] ($\times 10^{-3}$) mole/dL	9.41	24.53	3.69	1.206	46685	1.1347
		14.12	43.46	3.23	1.318	66191	1.9824
		18.82	46.79	1.98	1.134	43539	1.6139
		23.53	44.07	1.01	1.069	24949	1.7634
2	AIBN[b] ($\times 10^{-3}$) mole/dL	304.50	31.69	4.69	1.301	50792	1.4608
		456.75	52.89	4.36	1.342	61139	1.7569
		609.00	43.46	3.23	1.302	66191	1.9824
		761.25	38.76	1.53	1.221	57852	1.1190
3	Pressure[c] (psi)	1400	46.79	1.98	1.134	43539	1.6139
		1600	37.04	2.10	1.328	52452	1.3131
		1800	20.50	2.68	1.298	51403	1.2289
		2000	22.19	3.87	1.308	48311	1.4147
4	Temperature[d] (°C)	60	13.77	3.01	1.089	24470	1.6605
		70	24.70	4.35	1.345	31555	1.5744
		80	46.79	1.98	1.134	43539	1.6139
		90	43.15	1.21	1.211	49953	1.1190
5	Time[e] (h)	2	46.79	1.98	1.134	43539	1.6139
		4	46.63	0.79	1.108	42635	1.5423
		6	34.13	2.57	1.256	60162	1.2230
		8	33.27	2.76	1.287	69812	1.1246

[a] 80 ± 1°C, 1400 psi, [AIBN] 609.0 × 10^{-3} mol/dL, 2 h, [C60] 100 ± 1 mg.
[b] 80 ± 1°C, 1400 psi, [MMA] 14.12 × 10^{-3} mol/dL, 2 h, [C60] 100 ± 1 mg.
[c] 80 ± 1°C, [MMA] 18.82 × 10^{-3} mol/dL, [AIBN] 609.0 × 10^{-3} mol/dL, 2 h, [C60] 100 ± 1 mg.
[d] 1400 psi, [MMA] 18.82 × 10^{-3} mol/dL, [AIBN] 609.0 × 10^{-3} mol/dL, 2 h, [C60] 100 ± 1 mg.
[e] 80 + 1°C, 1400 psi, [MMA] 18.82 × 10^{-3} mol/dL, [AIBN] 609.0 × 10^{-3} mol/dL, [C60] 100 ± 1 mg.

RESULTS AND DISCUSSION

Polymerization of Methyl Methacrylate

A series of C60-PMMA conjugates were synthesized under different reaction conditions in $scCO_2$. The synthetic data show that AIBN-initiated polymerization of PMMA in the presence of C60 has been greatly influenced by supercritical conditions and concentration of AIBN and MMA respectively (Table I). This has in turn affected the recovery of C60 and rheoviscosity of the corresponding C60-PMMA conjugates. With increase in MMA concentration in the range $9.41–23.53 \times 10^{-3}$ mol/dL, corresponding polymerization increases but C60 used in conjugates decreases. With an increase in concentration of initiator ranging from 304.5 to 761.25×10^{-3} mol/dL, product yield gradually increased up to 52.89% and then decreased to 38.76%, probably due to AIBN initiator, which has a greater tendency to be combined with C60.[10] An increase in pressure and time caused a decrease of the yield of the product because fullerene 60 can inhibit the chain propagation by reacting with the initiator radical and/or by terminating the propagating chain at higher pressure, but in the case of temperature the highest yield was found at 80°C and after that the yield decreased. It has been reported that fullerene [60] reacts effectively with isobutyronitrile radicals produced by the thermal decomposition of AIBN.[10] Therefore, it is possible that C60 intercepts the initiating radicals in the polymerization reaction at higher temperature. These observations clearly indicate that AIBN-initiated polymerization of MMA in the presence of C60 has afforded the corresponding C60-PMMA conjugates at increasing yield with increase in AIBN concentration, probably due to the radicals from the initiator, which undergo multiple additions on C60, ultimately changing its nature sufficiently such that it would not inhibit polymerization.[11]

Rheoviscometry data show that due to the increasing integration of fullerene in polymers, the rheoviscosity increases. The progress of polymerization of MMA in the presence of C60 under different supercritical conditions has shown regular variations in the rheoviscosity of the resulting C60-PMMA conjugates. With increase in concentration of AIBN ranging from 304.5 to 761.25×10^{-3} mol/dL, the rheoviscosity changed from 1.221 to 1.342 (maximum value found at 456.75×10^{-3}) Mpa. An increase in temperature from 60° to 90°C contributed to an irregular variation in the rheoviscosity of the corresponding C60-PMMA conjugates. The decrease in the rheoviscosity was in the range of 2.349–1.322 Mpa s of the corresponding C60-PMMA conjugates. Such a decrease in rheoviscosity of the C60-PMMA conjugates may be due to homopolymerization of MMA instead of the formation of star structure under the investigated conditions.[15,20]

Gel Permeation Chromatography (GPC)

The GPC data of C60-PMMA are shown in Table I. The number-average molar mass varies from 24470 to 66191 g/mol with $PD < 2$. The number-average molar mass decreases with increase in MMA concentration from 102.5 to 205.0×10^{-3} mol/dL. The pressure has not shown so much effect on the number-average molar mass and PD of the polymer, but the temperature plays an important role in the case of number-average molar mass of C60-PMMA, which varies from 24470 to 49364 d/mol within the temperature range of 50°–90°C. AIBN concentration and time have moderate effect.[17,21]

Spectral Analysis

UV-vis spectra of MMA, PMMA, and C60-PMMA were recorded in THF. Pure C60 shows λmax at 256 nm with two broad peaks at 290 nm and 331 nm. PMMA shows λmax at 292 nm and the monomer MMA shows λmax at 290 nm as a weak band. As the C60 content increases from 1.98% to 4.69% in C60-PMMA polymer, λmax shifted from 293 to 297 nm, indicating a redshift due to $\pi \rightarrow \pi^*$ transition and a peak at 290 nm also present in C60-PMMA polymers. At 330 nm, a broad band of C60 was also found in C60-PMMA polymer between 329 and 331 nm due to $\pi \rightarrow \pi^*$ transition. These observations indicate an appropriate mixing of the wave function of C60-PMMA, which may cause the formation of star structure (Figure 1).[12,22]

FT-IR

In order to obtain structural information for the product, the PMMA-C60 conjugate polymer was analyzed by FT-IR. The characteristic band at 1731.87 cm^{-1} (very strong peak) corresponds to ester carbonyl (>C=O) group and the band around 1062.93–1388.01 cm^{-1} is a stretching vibration of C–O–C group. Absorption peaks at 1450.90 (ν C=C) and 2953.21 (υ C=C) are due to C60 content.[23] Disappearance of the peak (after polymerization) at 1650 cm^{-1}, which corresponds to the terminal methylene group of the monomer, clearly indicates the complete polymerization of the vinyl group (Figure 2).[13,25]

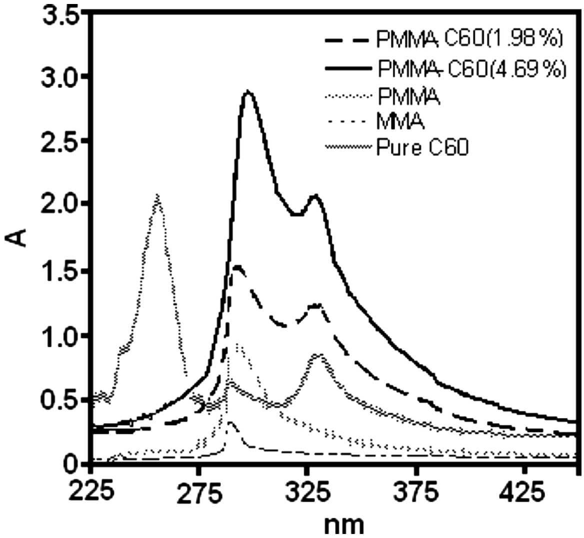


Figure 1. UV-vis spectra of pure C60, MMA, PMMA, and C60-PMMA.

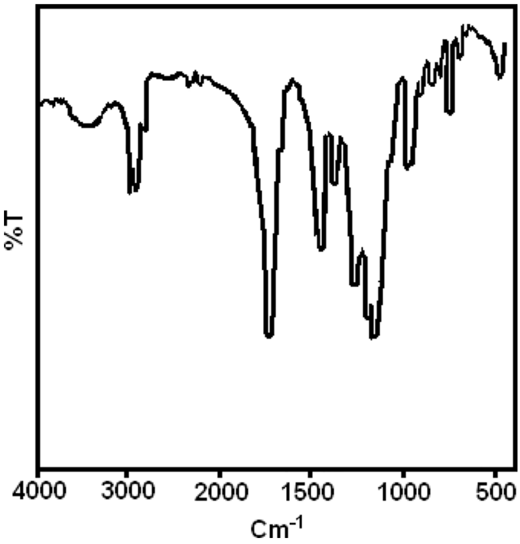


Figure 2. FT-IR spectrum of C60-PMMA.

^{1}H NMR

The ^{1}H NMR spectrum of C60-PMMA in $CDCl_3$ is shown in Figure 3. Here, all the proton resonance signals correspond to PMMA such as 0.77, 0.95 ($-CH_3$ for syndiotactic and heterotactic configuration, respectively), and 1.80–2.10 ppm ($-CH_2-$).[17] The main feature of the ^{1}HNMR spectrum is the peak corresponding

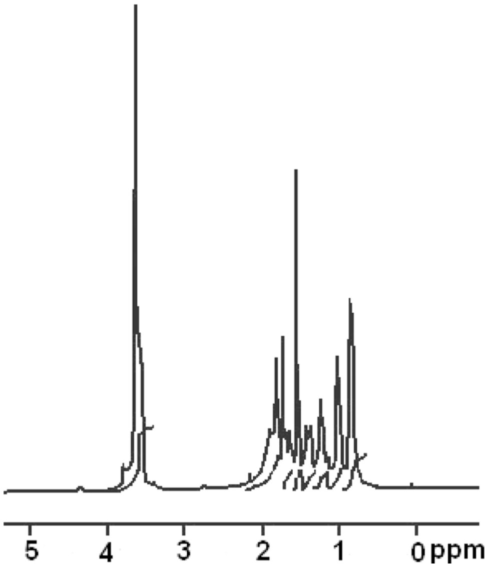


Figure 3. ^{1}H NMR spectrum of C60-PMMA.

to the methoxy carbon ($-OCH_3$) at $\delta = 3.53$–3.76, which confirms the PMMA microsphere.[25,26]

^{13}C NMR

The ^{13}C NMR spectrum of PMMA shows all the peaks corresponding to carbon atoms in different environments in the polymer structure. The methylene group ($-CH_2-$) shows a peak at 54.597 ppm and the quarternary carbon (>C<) and carbonyl carbon group (>C=O) give characteristic peaks around 44.753 and 178.078 ppm, respectively. Similarly, methyl carbon ($-CH_3$) and methoxy carbon ($-OCH_3-$) show peaks at 18.903 and 52.052 ppm, respectively. The C60 shows a large peak at 77.258 ppm. The other peaks were associated with the impurities (Figure 4).[24]

Thermal Characterization

Thermal stability and degradation patterns were determined by employing thermogravimetric analysis (TG). The best characteristic of the change of thermal stability is the temperature shift of the entire TG curve (or the middle part of it), but not the shift of onset or the starting temperature of the mass loss. During the oxidative degradation in air of PMMA, three processes occur practically simultaneously: thermal degradation or scission of chains; oxidation, or insertion of oxygen atoms in the polymer chains and in products of the degradation; and a sublimation of degradation products.[19] The TG spectrum of PMMA in Figure 5(a) shows two onset temperatures, at 166.29°C and 360.26°C, respectively, and end-set temperature at 441.42°C. The thermogram indicates 20% thermal degradation of polymer at 228.12°C with 0.0069 mg/°C decomposition rate, 40% degradation at 276.24°C with 0.029 mg/°C decomposition rate, and 60% and 80% degradation at 320.02°C and 403.46°C with 0.0321 mg/°C and 0.0168 mg/°C decomposition rates, respectively. At 600°C, 0.96% residues are found (see Table II).[24] C60-PMMA

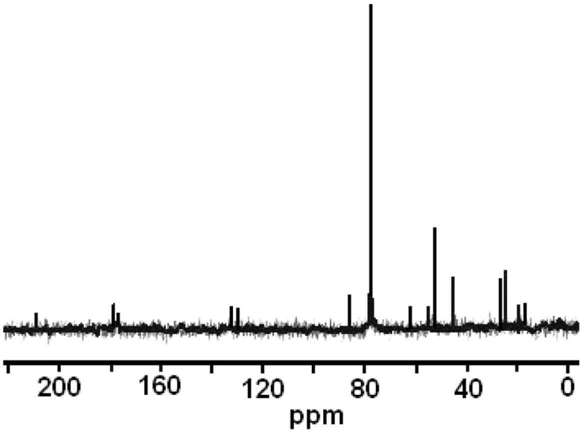
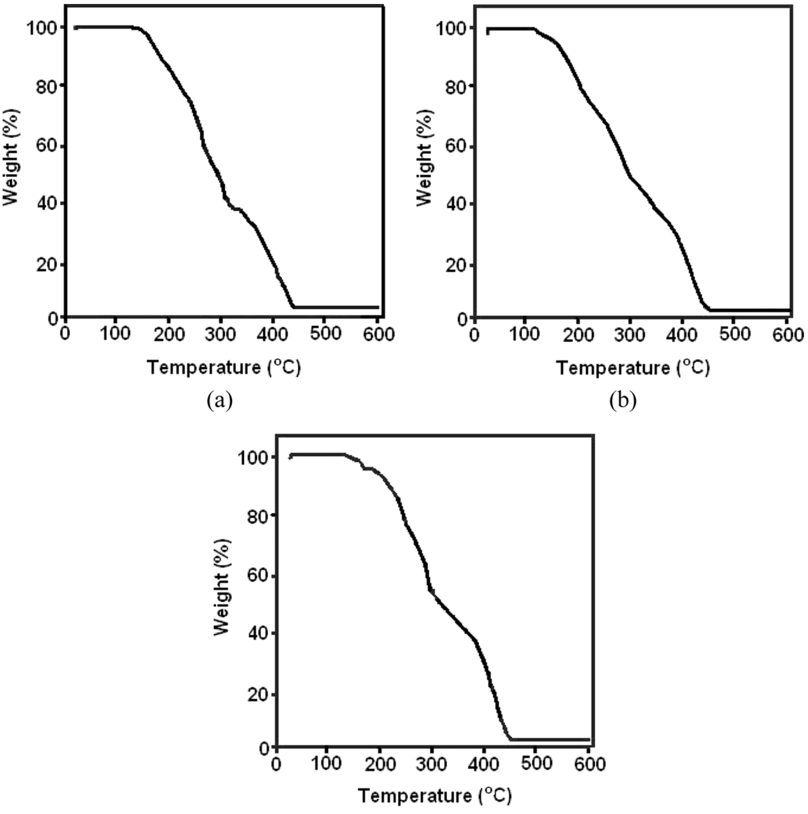


Figure 4. ^{13}C NMR spectrum of C60-PMMA.



(a) (b)

(c)

Figure 5. TG thermograms of (a) PMMA, (b) C60-PMMA (1.01%), and (c) C60-PMMA (3.23%).

(1.01%) shows two onset temperatures at 205.18°C and 390.55°C respectively and end-set temperature at 442.50°C. The thermogram indicates 20% thermal degradation of C60-polymer at 247.23°C with 0.0066 mg/°C decomposition rate, 40% degradation at 293.82°C with 0.0319 mg/°C decomposition rate, and 60% and 80% degradation at 372.68°C and 418.91°C with 0.0187 mg/°C and 0.0321 mg/°C decomposition rates, respectively (Figure 5(b), Table II). C60-PMMA (3.23%) shows only one onset temperature at 157.82°C and end-set temperature at 452.99°C. The thermogram shows 20% thermal degradation of C60-polymer at 214.78°C with

Table II. TG of PMMA and C60-PMMA

	Weight residue (%) at temperature (°C)					
Polymer	20	40	60	80	100	Char yield (%)
PMMA	403.46	320.07	276.23	228.12	22.34	0.96
C60-PMMA (1.01%)	418.91	372.68	293.82	247.23	22.52	2.13
C60-PMMA (3.23%)	423.56	361.76	297.19	214.78	24.21	3.79

0.0078 mg/°C decomposition rate, 40% degradation at 297.19°C with 0.0178 mg/°C decomposition rate, and 60% and 80% degradation at 361.76°C and 423.56°C with 0.0231 mg/°C and 0.0241 mg/°C decomposition rates, respectively (Figure 5(c), Table II).[27]

CONCLUSIONS

Polymethyl methacrylate (PMMA)-C60 conjugates were synthesized through 2,2-azobisisobutyronitrile-initiated in situ polymerization of MMA under a series of reaction conditions in $scCO_{2.}$ Polymerization of MMA in C60 progressed with increase in rheoviscosity with concentration of AIBN and temperature under applied supercritical conditions. Presence of C60 in PMAA was ascertained through FT-IR and UV-vis spectra. The UV-vis and ^{13}C NMR spectra indicate the formation of C60-PMMA as star structure. These observations clearly indicate that after C60 doping, the thermal degradation temperature increases at all stages. The C60-PMMA conjugates have shown improved thermal stability at higher temperature with respect to PMMA. Char yield also increases due to C60 content.

REFERENCES

1. Nalawade, S. P., F. Picchioni, and L. P. B. M. Janssen. 2006. Supercritical carbon dioxide as a green solvent for processing polymer melts: Processing aspects and applications. *Prog. Polym. Sci.* 31: 19–43.
2. Ganapathy, H. S., M. H. Woo, S. Hong, and K. T. Lim. 2007. Supercritical carbon dioxide assisted impregnation of molsidomine into poly(DL-Lactic-co-glycolide) for sustained release application. *Key Eng. Mater.* 342–343: 501–504.
3. Hu, X., and A. J. Lessery. 2006. Solid-state processing of polymer in the presence of supercritical carbon dioxide. *J. Cell. Plast.* 42: 517.
4. Wang, W., S. M. Howdle, and D. Yan. 2005. One-step seed dispersion polymerization in supercritical carbon dioxide. *Chem. Commun.* (31): 3939–3941.
5. Liu, Z., X. Dai, J. Xu, B. Han, J. Zhang, Y. Wang, Y. Huang, and G. Yang. 2004. Encapsulation of polystyrene within carbon nanotubes with the aid of supercritical CO_2. *Carbon* 42 (2): 458–460.
6. Chen, Y., Z. E. Huang, R. F. Cai, S. Q. Kong, S. M. Chen, and Q. F. Shao. 1996. Synthesis and characterization of soluble C60 chemically modified poly(p-bromostyrene). *J. Polym. Sci. Polym. Chem.* 34 (16): 3297.
7. Kuo, C., J. Kumar, S. K. Tripathy, Y. Long, and J. Chiang. 2001. Synthesis and properties of [60] fullerene-polyvinyl pyridine conjugates for photovoltaic devices. *J. Macromol. Sci. Pure Appl. Chem. A* 38 (12): 1481–1498.
8. Chen, Y., R. F. Cai, Z. E. Huang, and S. Q. Kong. 1995. A novel and versatile method for the synthesis of soluble fullerenated polymers. *Polym. Bull.* 35 (6): 705.
9. Cai, R. F., X. Bai, Y. Chen, and Z. E. Huang. 1998. Preparation and structural characterization of C70 chemically modified poly(N-vinylcarbazole). *Eur. Polym. J.* 34 (1): 7–12.
10. Mehrotra, S., A. Nigam, and R. Malhotra. 1997. Effect of [60] fullerene on the radical polymerization of alkenes. *Chem. Commun.* (5): 463–464.
11. Camp, A. G., A. Lary, and W. T. Ford. 1995. Free-radical polymerization of methyl methacrylate and styrene with C60. *Macromolecules* 28: 7959.
12. Wang, C., Z. Guo, S. Fu, W. Wu, and D. Zhu. 2004. Polymers containing fullerene or carbon nanotube structures. *Prog. Polym. Sci.* 29: 1079–1141.

13. Hems, W. P., T. M. Yong, J. L. M. Nunen, A. I. Cooper, A. B. Holmes, and D. A. Griffin. 1999. Dispersion polymerisation of methyl methacrylate in supercritical carbon dioxide—Evaluation of well defined fluorinated AB block copolymers as surfactants. *J. Mater. Chem.* 9: 1403–1407.
14. Kropka, J., and P. Green. 2006. Structure and properties of poly(methyl methacrylate) (PMMA)-fullerene (C_{60}) nanocomposites. Paper presented at the American Physical Society, APS March Meeting, March 13–17.
15. Agarwal, V., M. G. H. Zaidi, S. Vishnoi, S. Alam, and A. K. Rai. 2009. Fullerene [60] mediated polymerization and characterization of polyacrylic acid in supercritical carbon dioxide. *Int. J. Polym. Anal. Charact.* 14: 1–15.
16. Choi, C. H., and M. Kertesz. 2000. Vibrational assignment of all 46 fundamentals of C60 and $C60^{6-}$: Scaled quantum mechanical results performed in redundant internal coordinates and compared to experiments. *J. Phys. Chem. A* 104: 102–112.
17. Guo, Z., G. Yang, Z. Huang, and Z. Huang. 2001. Synthesis and characterization of a diblock copolymer of methyl methacrylate and vinyl acetate by successive photo-induced charge transfer polymerization using ethanolamine as the parent compound. *Macromol. Rapid Commun.* 22: 120–125.
18. Arndt, K. F., A. Richter, S. Ludwig, J. Zimmermann, J. Kressler, D. Kuckling, and H. J. Adler. 2000. Poly(vinyl alcohol)/poly(acrylic acid) hydrogels: FT-IR spectroscopic characterization of crosslinking reaction and work at transition point. *Acta Polym.* 50 (11): 383.
19. Ginzburg, B. M., L. A. Shibaev, V. L. Ugolkov, and V. P. Bulatov. 2003. Influence of C_{60} fullerene on the oxidative degradation of a free radical poly(methyl methacrylate). *J. Macromol. Sci. Part B* 42 (1): 139–166.
20. Gombos, Z. N., V. Nagy, L. Mihály Vas, and J. Gaál. 2005. Investigation of pore size and resin absorbency in chopped strand mats. *Period. Polytech. Ser. Mech. Eng.* 49 (2): 131–148.
21. Ford, W. T., and T. D. Graham. 1997. Incorporation of C_{60} into poly(methyl methacrylate) and polystyrene by radical chain polymerization produces branched structures. *Macromolecules* 30 (21): 6422–6429.
22. Jiang, G. C., W. C. Guan, and Q. X. Zheng. 2004. Synthesis of fullerene-acrylamide copolymer nanoball and its lubrication properties. *Chin. J. Chem.* 22: 877–881.
23. Morita, S., A. A. Zakhidov, and K. Yoshino. 1992. Doping effect of buckminsterfullerene in conducting polymer—Change of absorption spectrum and quenching of luminescence. *Solid State Commun.* 82 (4): 249–252.
24. Sankar, V., T. S. Kumar, and K. P. Rao. 2004. Preparation, characterisation and fabrication of intraocular lens from photo initiated polymerised poly (methyl methacrylate). *Trends Biomater. Artif. Organs* 17 (2): 24–30.
25. Balamurugan, A., S. Kannan, V. Selvaraj, and S. Rajeswari. 2004. Development and spectral characterization of poly(methyl methacrylate)/hydroxyapatite composite for biomedical applications. *Trends Biomater. Artif. Organs* 18 (1): 41–45.
26. Shi, Y., Z. F. Fu, Y. D. Zhang, and S. K. Jiao. 2003. Synthesis of comblike poly(methyl methacrylate) by atom transfer radical polymerization with poly(ethyl 2-bromoacrylate) as macroinitiator. *Chin. Chem. Lett.* 14 (12): 1289–1292.
27. Hussain, R., and D. Mohammad. 2004. X-ray diffraction study of the changes induced during the thermal degradation of poly (methylmethacrylate) and poly (methacryloyl chloride). *Turk. J. Chem.* 28: 725–729.