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### Fullerene [60]-Mediated Polymerization of Polyacrylic Acid in Supercritical Carbon Dioxide

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## Fullerene [60]-Mediated Polymerization of Polyacrylic Acid in Supercritical Carbon Dioxide

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**Abstract:** A series of fullerene [60]-polyacrylic acid (C60-PAA) conjugates was synthesized through 2,2-azobisisobutyronitrile (AIBN)-initiated in situ polymerization of acrylic acid (AA) under different reaction conditions in supercritical (carbon dioxide (scCO<sub>2</sub>)). This has afforded corresponding C60-PAA conjugates with C60 content ranging from 0.76 to 6.69% and rheoviscosity from 1.183 to 2.349 Mpas (means—in this investigation, fullerene [60] content varied from 0.76 (minimum) to 6.69% (maximum) in synthesized C60-PAA conjugates and rheoviscosity varied from 1.183 (minimum) to 2.349 Mpas (maximum value). The process of in situ polymerization was monitored at concentrations (mole/dL) of AIBN of  $304.50\text{--}931.5 \times 10^{-3}$  and AA of  $6.94\text{--}20.82 \times 10^{-3}$ , temperatures of 50°–90°C, pressures of 1000–2600 psi, and times of 2–26 h. The progress of in situ polymerization was monitored rheoviscometrically in methanol at  $25^\circ \pm 1^\circ\text{C}$  and by gel permeation chromatography. Selected C60-PAA conjugates were characterized by UV-vis, FT-IR, <sup>1</sup>H NMR, laser-induced breakdown spectra (LIBS),

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transmission electron microscopy (TEM), and simultaneous thermogravimetric-differential thermogravimetric analysis-differential scanning calorimetry (TG-DTA-DSC) in nitrogen.

**Keywords:** C60-polyacrylic acid conjugates; Characterization; Supercritical carbon dioxide; Synthesis

## INTRODUCTION

Over the past few decades, supercritical fluids, including supercritical carbon dioxide (scCO<sub>2</sub>), have gained significant technological advantages due to their gas-like diffusivity and liquid-like density. The unique property of diffusion of scCO<sub>2</sub> increases the free volume and mobility of the polymer chains with simultaneous reductions in the glass transition temperature ( $T_g$ ) and viscosity. This has opened opportunities to synthesize and process a variety of materials ranging from nanoparticles to polymer-based composites with enhanced mechanical, thermal, and electrical properties,<sup>[1,2]</sup> but very few studies have been reported on synthesizing fullerene and carbon nanotube conjugated polymers in scCO<sub>2</sub>.<sup>[3]</sup>

The synthesis and isolation of macroscopic quantities of fullerene [60] have stimulated great interest in fullerene polymers. These macromolecular fullerene derivatives are synthesized through either a direct copolymerization of fullerenes with monomers in the presence of radical initiators,<sup>[4,5]</sup> functionalization of fullerenes to give a polymerizable monomer and then use of this monomer to conduct copolymerization with other monomers, and/or reacting functionalized polymers with fullerenes.<sup>[6]</sup> In the past few years, a number of studies have been done to synthesize water-soluble fullerenated polymers by reacting various vinyl monomers, e.g., polystyrene sulfonate,<sup>[7]</sup> 4-vinylpyridin,<sup>[4]</sup> vinylbenzylchloride,<sup>[8]</sup> N-vinylcarbazole,<sup>[9]</sup> and vinylpyrrolidone.<sup>[10]</sup>

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

We report here findings of our study on AIBN-initiated radical polymerization of a range of acrylic acids in the presence of fullerene [60] where supercritical carbon dioxide was used as the reaction medium. The objective of this study was to determine how general the inhibition of radical polymerization by fullerene [60] is and to discover the role of the different reaction conditions in the polymerization.

## EXPERIMENTAL SECTION

### Starting Materials

The C60 ( $\geq 99.5\%$ ) was purchased from SES Research (Houston, USA). Acrylic acid was purchased from Acros Chemicals (USA). AIBN was purchased from Himedia Chemicals (India). Other chemicals were used of AR grade. Carbon dioxide (99.9%) was used as supercritical solvent.

### Synthesis of C60-Containing Polymers in $\text{scCO}_2$

All C60-PAA conjugates were synthesized in a stainless steel high-pressure reactor (100 cm<sup>3</sup>), model MC 10 10 SI ST equipped with a proportional-integral-derivative (PID) temperature controller, manufactured by PPI (Warminster, Penn., USA).<sup>[16,17]</sup> 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 at a temperature ranging from 50° to 90°±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  $\text{scCO}_2$  over 2 to 26 h. The cell was then cooled to 25°±1°C, and the CO<sub>2</sub> was vented into dichloromethane. The cell was opened to obtain C60-PAA conjugates (Table I).

### Characterization

Rheoviscometry measurements were carried out on a Nach Hoppler Viscometer (Germany). Viscosity was derived from the resistance against the solution of corresponding C60-containing polymers with their homopolymer solutions as a reference. The time when the ball sinks 30 mm deep in the cuvette was measured.<sup>[18]</sup> UV-vis spectra were recorded with a spectrophotometer, model Genesis 10 Thermospectronic (USA).<sup>[19]</sup> The

**Table I.** Synthesis of PAA-C60 under different reaction conditions in scCO<sub>2</sub>

No.	Variables	Variations	Yield (%)	C60 (%)	Rheoviscosity (MPa s)
1	AA <sup>a</sup> ( $\times 10^{-3}$ ) mole/dL	6.94	83.27	4.34	2.349
		10.41	80.10	2.80	1.937
		13.88	82.94	1.61	1.730
		17.35	80.07	1.79	1.593
		20.82	88.22	1.65	1.510
2	AIBN <sup>b</sup> ( $\times 10^{-3}$ ) mole/dL	304.50	83.07	1.79	1.526
		456.75	84.50	1.71	1.639
		609.00	86.25	1.67	1.784
		761.25	88.57	1.45	1.863
		931.5	92.38	1.31	1.777
3	Pressure <sup>c</sup> (psi)	1000	5.34	0.76	1.183
		1400	83.27	4.34	1.756
		1800	73.50	4.54	1.674
		2200	57.32	5.43	1.492
		2600	56.80	5.30	1.321
4	Temperature <sup>d</sup> (°C)	50	61.75	3.15	1.859
		60	83.27	4.34	2.349
		70	75.30	6.43	1.818
		80	64.42	6.69	1.844
		90	73.23	6.41	1.557
5	Time <sup>e</sup> (h)	2	83.27	4.34	2.349
		8	63.34	5.05	1.777
		14	43.16	5.41	1.535
		20	38.14	6.05	1.418
		26	30.99	6.37	1.322

<sup>a</sup>60° ± 1°C, 1400 psi, [AIBN] 304.5 × 10<sup>-3</sup> mole/dL, 2 h, [C60] 100 ± 1 mg.

<sup>b</sup>60° ± 1°C, 1400 psi, [AA] 17.35 × 10<sup>-3</sup> mole/dL, 2 h, [C60] 100 ± 1 mg.

<sup>c</sup>60° ± 1°C, [AA] 6.94 × 10<sup>-3</sup>, [AIBN] 304.5 × 10<sup>-3</sup> mole/dL, 2 h, [C60] 100 ± 1 mg.

<sup>d</sup>1400 psi, [AA] 6.94 × 10<sup>-3</sup>, [AIBN] 304.5 × 10<sup>-3</sup> mole/dL, 2 h, [C60] 100 ± 1 mg.

<sup>e</sup>60° ± 1°C, 1400 psi, [AA] 6.94 × 10<sup>-3</sup>, [AIBN] 304.5 × 10<sup>-3</sup> mole/dL, [C60] 100 ± 1 mg.

molecular weights were measured by using a Varian Pro Star gel permeation chromatography (GPC) apparatus equipped with a 355 RI detector by using tetrahydrofuran (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 of 37°C. Fourier transform-infrared (FT-IR) spectra were recorded on Bucker FT-IR Spectrophotometer in KBr.<sup>[20]</sup> A Q-switched Nd:YAG laser (Quanta Ray) emitting at 1,064 nm, with 28 nanoseconds pulse duration was used for the characterization of C60, polymers, and

corresponding C60-polymer derivatives.<sup>[21]</sup> Electron micrographs of gold-coated, samples were scanned at 4.00 KX on a LEO-435 scanning electron microscope (SEM).<sup>[22]</sup> Simultaneous differential thermogravimetric-thermogravimetric-differential thermal analysis (DTG-TG-DTA) was performed on Netzsch-Geratebau GmbH thermal analyzer model STA-409 in static air at 25°C/10 (K/min)/1000°C.

## RESULTS AND DISCUSSION

### Polymerization of Acrylic Acid

A series of C60-PAA conjugates were synthesized under different reaction conditions in scCO<sub>2</sub>. The synthesis data show that AIBN-initiated polymerization of AA in the presence of C60 was greatly influenced by supercritical conditions and concentration of AIBN and AA (Table I). This in turn affected the recovery of C60 and rheoviscosity of the corresponding C60-PAA derivatives. With increase in AA at concentrations ranging from 6.94 to 20.82 × 10<sup>-3</sup> mol/dL, the corresponding polymerization degree increases, but C60 obtained in product in decreasing order was 4.80–1.65, due to the high amount of the required concentration of the initiator. With increase in concentration of the initiator ranging from 304.5 to 931.5 × 10<sup>-3</sup> mol/dL, product yield was gradually increased ranging from 83.07 to 92.38% due to the fact that radicals from the initiator undergo multiple additions on fullerene [60], ultimately changing its nature sufficiently such that it would not inhibit polymerization.<sup>[10]</sup> Increase in pressure, time, and temperature caused decreasing effect over the yield of the product. The reason is that C60 can inhibit the chain propagation by reacting with the initiator radical and/or by terminating the propagating chain at higher temperature and pressure. It has been reported that C60 reacts effectively with isobutyronitrile radicals produced by the thermal decomposition of AIBN.<sup>[10]</sup> 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 AA in the presence of C60 has afforded the corresponding C60-PAA conjugates at increasing yield with increase in AIBN concentration, probably due to the radicals from the initiator, which undergo multiple additions on C60, ultimately by changing its nature sufficiently that it would not inhibit the polymerization.<sup>[11]</sup>

Rheoviscometry data show that due to increasing impregnation of C60 in polymers the rheoviscosity increases. The progress of polymerization of AA in the presence of C60 under different supercritical conditions has shown regular variations in the rheoviscosity of the resulting C60-PAA conjugates with increase in AIBN concentration. With increase

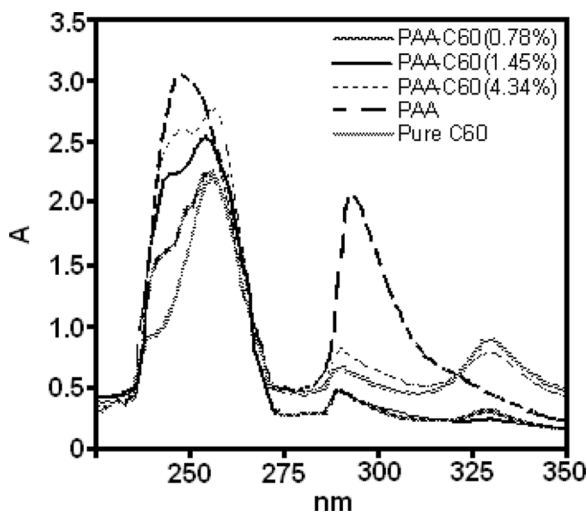
in concentration of AIBN ranging from 304.5 to  $761.25 \times 10^{-3}$  mol/dL a regular increase in rheoviscosity ranging from 1.526 to 1.863 Mpa s of corresponding conjugates was observed.

This showed corresponding rheoviscosity ranging from 1.859 to 2.349 Mpa s. Increase in time decreased in the rheoviscosity ranging from 2.349 to 1.322 Mpa s of the corresponding C60-PAA conjugates.<sup>[12]</sup> Such decrease in rheoviscosity of the C60-PAA conjugates may be due to homopolymerization of AA in place of the formation of star structure under the investigated conditions (Table I).

### Spectral Analysis

UV-vis spectra of pure C60, PAA, and C60-PAA were recorded in tetrahydrofuran. Pure C60 shows  $\lambda_{\max}$  at 256.28 nm with two broad peaks at 290 and 331 nm. PAA shows  $\lambda_{\max}$  at 248 nm and a peak at 293 nm. As the C60 content increases from 0.78 to 4.34% in C60-PAA polymer the  $\lambda_{\max}$  is shifted from 257 to 251 nm, indicating a blue-shift due to  $n \rightarrow \pi^*$  transition and the peak at 290 nm is also present in C60-PAA. At 330 nm, a broad band of C60 was also found in C60-PAA polymer; between 327 and 331 nm it is due to  $n \rightarrow \pi^*$  transition<sup>[13,14]</sup> (see Figure 1).

In order to obtain structure information on the product, the structure of C60, PAA, and C60-PAA was analyzed by FT-IR. Pure C60 exhibits characteristic absorptions corresponding to  $\nu$  C-C (1426.49),  $\nu$  C=C (2922.5), and  $\nu$  C=C=C (1655.05).<sup>[15,16]</sup> The  $\nu$ (COOH) absorption in



**Figure 1.** UV-vis spectra of pure C60, PAA, and C60-PAA.

the bulk PAA appeared at approximately  $1700\text{ cm}^{-1}$ ; this band is due to self-association between the acid groups in the polymer matrix; the  $1580$  and  $1640\text{ cm}^{-1}$  peaks are due to the  $\text{COO}^-$  ion with two free polarized AA stretching bands at  $1554.0$  and  $1449.8\text{ cm}^{-1}$ . Whereas C60-PAA has shown absorptions corresponding to  $\text{CH}_2$  ( $\nu_s$ ;  $2921.60$ ),  $\nu\text{ C=O}$  ( $1729.90$ ),  $\nu\text{ C=C}$  (disubstituted alkenes,  $1666.6$ ),  $\nu\text{ C=C=C}$  ( $1645.1$ ),  $\delta\text{ C-(C=O)-C}$  (bending,  $1255.2$ ), and  $\text{C-H}$  (bending,  $1020.4$ ), the  $1580$  and  $1640\text{ cm}^{-1}$  peaks are due to the  $\text{COO}^-$  ion with two free polarized stretching bands at  $1553.3$  and  $1449.8$ <sup>[17,18]</sup> (Figure 2).

The  $^1\text{H}$  nuclear magnetic resonance (NMR) spectrum of C60-PAA in  $\text{D}_2\text{O}$  is shown in Figure 3. In this spectrum, the signal of terminal  $=\text{CH}_2$  appears at  $0.9310$  and  $0.9136$  ppm. There is a pentet at  $2.4619$  ppm due to the presence of terminal  $(=\text{CH}(\text{COOH})-)$  group. The quartet at  $3.7067$  ppm indicates the presence of  $-\text{CH}$  of polymeric chain. The  $-\text{CH}_2-$  group of polymer chain shows a triplet at  $2.6286$  ppm and the rest of the peaks are due to the impurities.<sup>[19]</sup>

Characteristic laser-induced breakdown spectra (LIBS) absorption (nm) corresponding to medium-intensity lines for Na ( $317.25$ ,  $318.75$ ) and Si ( $232.5$ ,  $255.25$ ,  $262.5$ ) and low-intensity lines for silicon ( $393.75$ ,  $397.5$ ) were observed for glass spectra. LIBS of C60 showed medium-intensity lines at  $270$ ,  $283.8$ ,  $427.374$ , and  $229.592$ , low-intensity lines at  $393.75$  and  $396.25$  for Si, and a medium-intensity line for Na  $318.25$  with a high-intensity line at  $248$ , indicating the presence of C60 in glass substrate (Figure 4). LIBS of PAA and corresponding C60-polymers

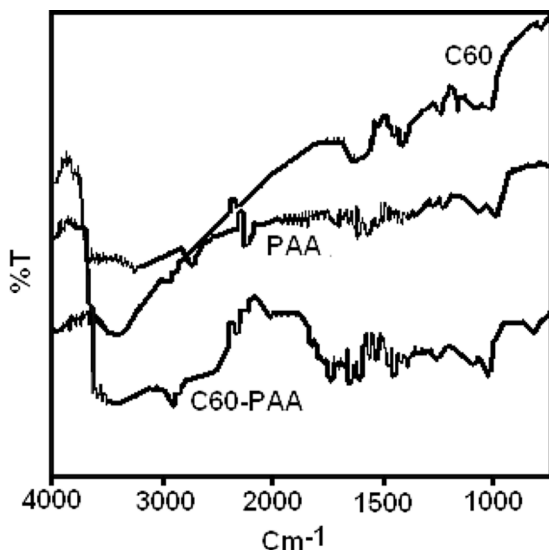


Figure 2. FT-IR spectra.



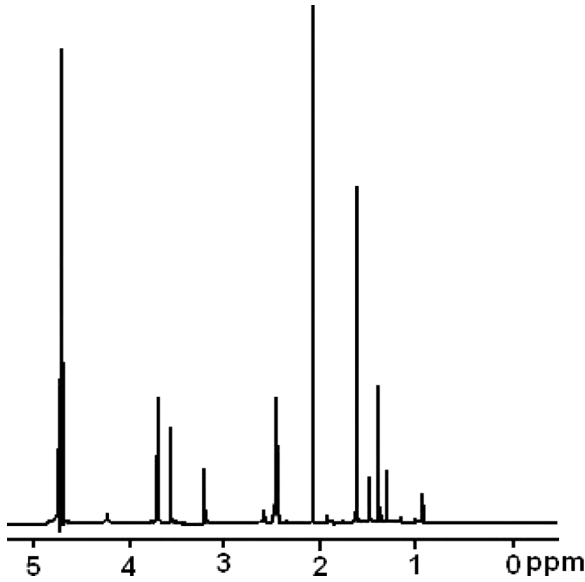


Figure 3. <sup>1</sup>H NMR spectrum of C60-PAA.

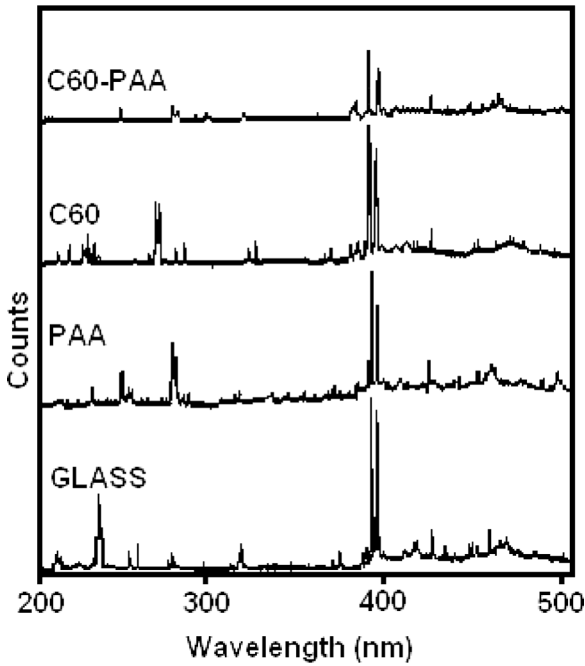


Figure 4. LIBS spectra.

showed absorptions corresponding to carbon, sodium, and silicon common to that of C60 in glass substrate with the additional absorption corresponding to O(II) 396.66, 464.8, H 434.691<sup>[20,21]</sup> (Figure 4).

### Thermal Characterization

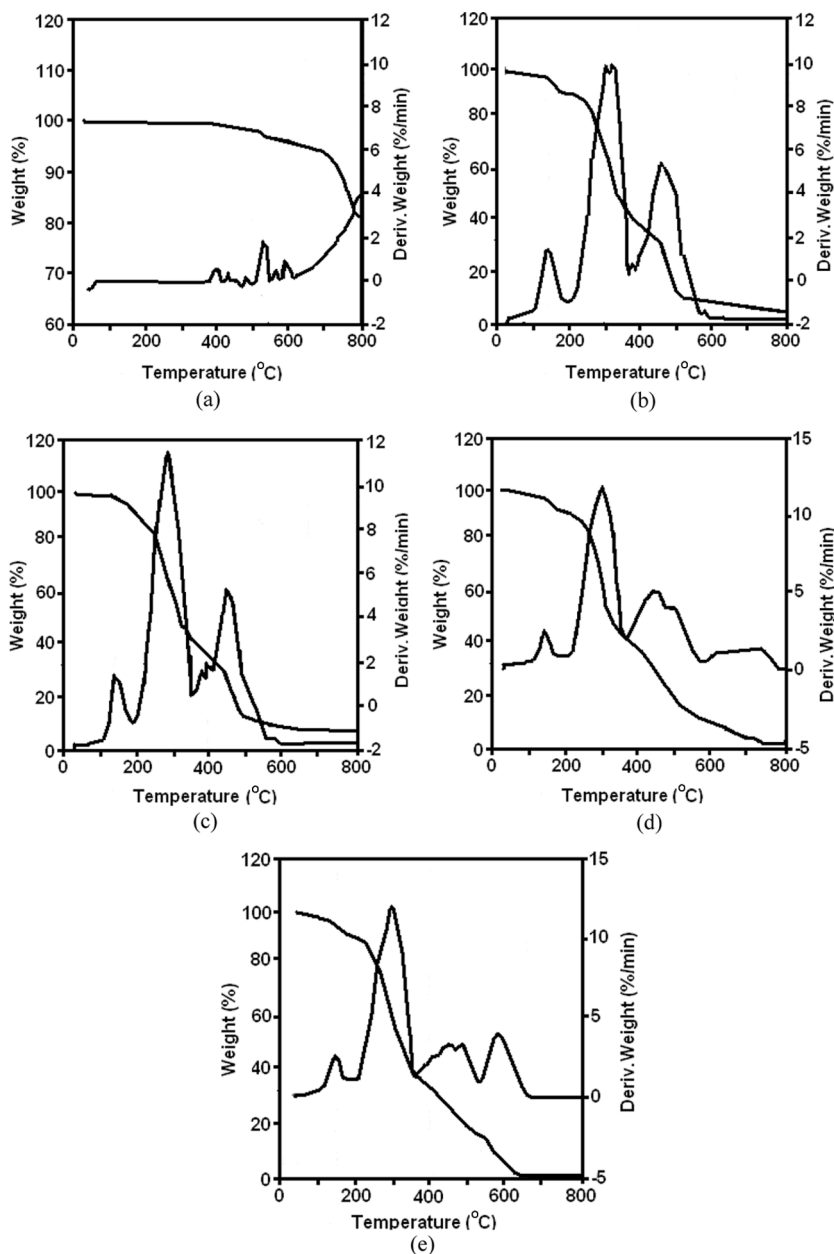
Thermal stabilities and degradation patterns were determined by employing thermogravimetric analysis (TG-DTA). Pure C60 first-stage decomposition started at 365.35°C, and up to 800°C the total weight loss was 18.30% (Figure 5(a)).

PAA exhibits two-step decomposition. The first stage started at 192.30°C with 0.0394 mg/°C decomposition rate. The total weight loss at this stage was 47.92%. Under this temperature, a weight loss of 8.452% was due to the moisture and solvent content in PAA. The second stage started at 374.98°C, and the weight loss was 36.77% with 0.0197 mg/°C decomposition rate. DTA confirmed the previous observation with a broad peak at 456.60°C (Figure 5(b)). In the case of C60-PAA (0.78% C60), the first decomposition stage started at 184.60°C, leading to 49.85% weight loss. The second stage started at 357.75°C, and the total weight loss at this stage was 33.55%. DTA confirmed this observation with a peak at 452.29°C (Figure 5(c)). On the other hand, 1.45% and 4.34% C60-containing polymers show three-step decompositions. The new last, third stage appeared at 576.90°C and 532.75°C with the total weight loss of 10.37% and 14.90%, respectively (Figure 5(d), (e)). These observations clearly indicate that with the increased C60 content in polymers the weight loss of PAA at the second stage was decreased and a new third stage appeared. The C60-PAA polymers have shown an improved thermal stability at higher temperature with respect to PAA. Char yield decreased with increasing percent of C60 in polymers<sup>[22]</sup> (Table II).

DSC profiles of PAA and C60-PAA were studied with reference to pure C60. They exhibited a single transition point appearing as DSC endotherm at 396.99°C (Figure 6(a)). PAA showed  $T_g$  at 183.02°C and  $T_m$  at 255.29°C (Figure 6(b)). With an increase in C60 content, a regular change in the DSC endotherm was observed with profiles corresponding to  $T_g$  and  $T_m$  in all cases (Figures 6(c) and (d)). The C60-PAA with C60 4.34% showed two glass transition temperatures,  $T_{g1}$  at 78.82°C and  $T_{g2}$  at 137.84°C, respectively and  $T_m$  at 255.16°C<sup>[23]</sup> (Figure 6(e); Table III).

### Morphology

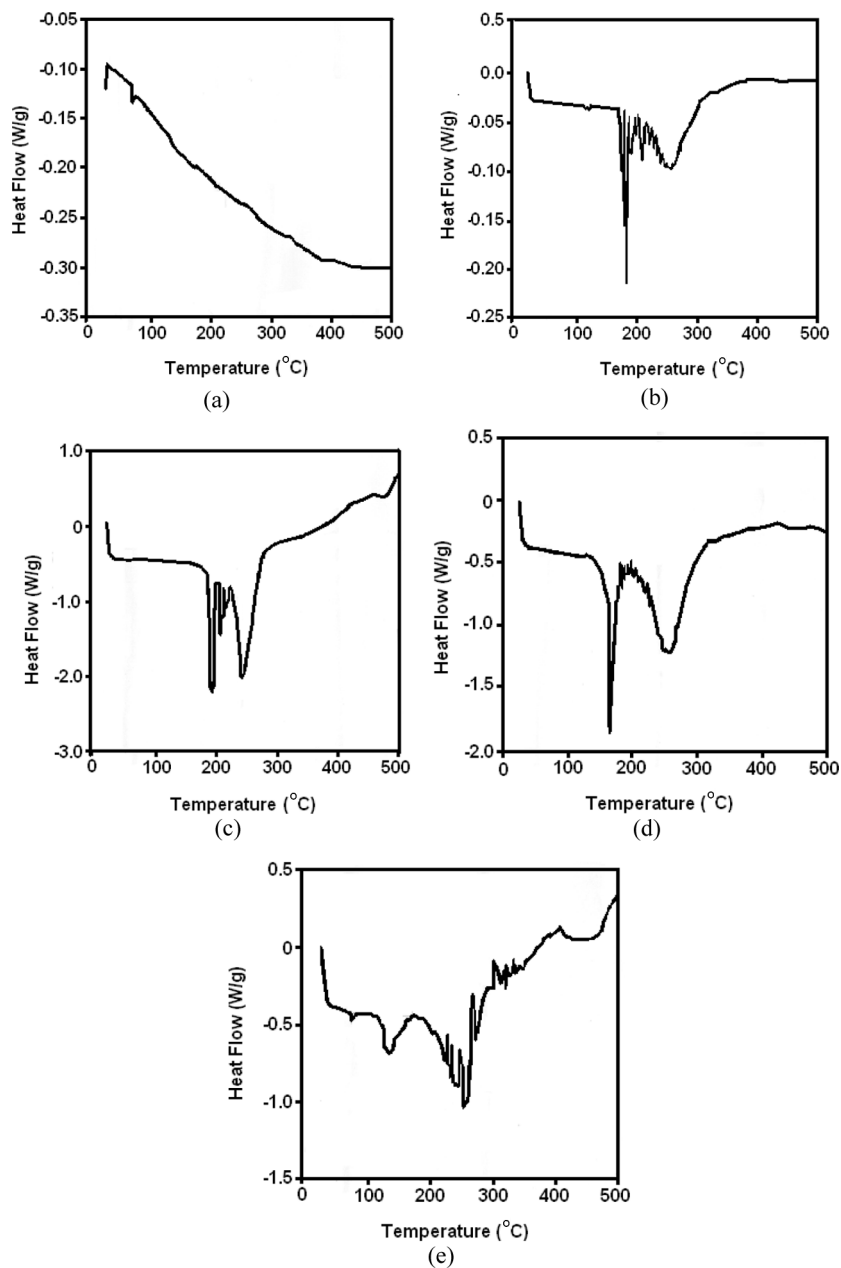
Effect of C60 content on the morphology of corresponding C60-polymers was evaluated by comparative SEM. Impregnation of C60 into respective polymers rendered corresponding C60-polymers with the enhanced



**Figure 5.** (a) TG-DTA spectrum of pure C60; (b) TG-DTA spectrum of PAA; (c) TG-DTA spectrum of C60-PAA (0.78%); (d) TG-DTA spectrum of C60-PAA (1.45%); and (e) TG-DTA spectrum of C60-PAA (4.34%).

**Table II.** TG-DTA of C60, PAA, and C60-PAA

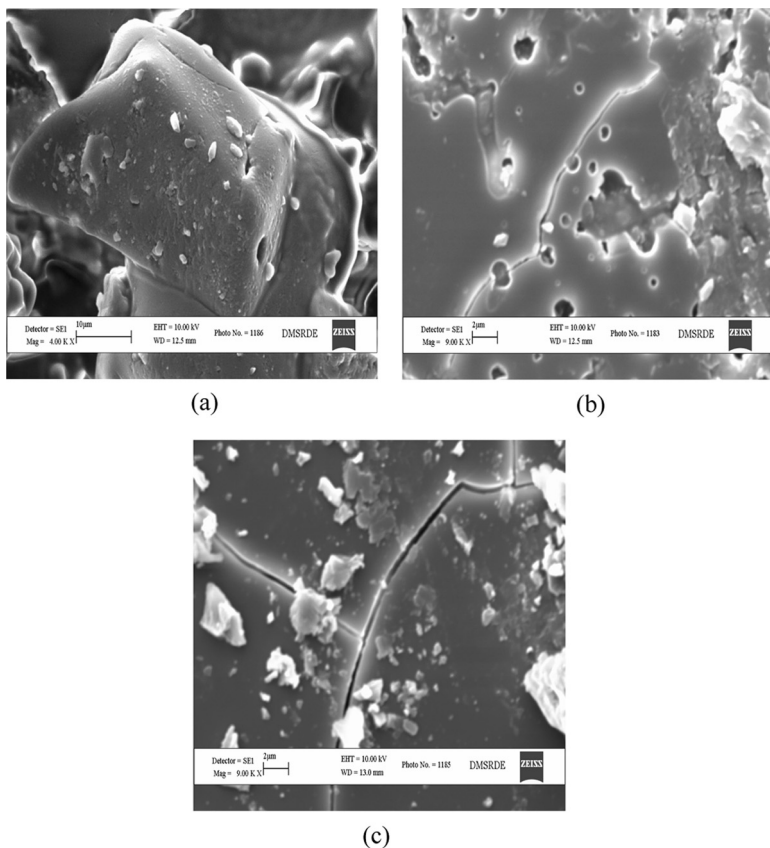
Polymer	Weight residue (%) at temperature (°C)							Char yield (%)	DTA (°C)
	20	40	60	80	100	>800	DTA (°C)		
C60	—	—	—	—	—	—	23.10	—	—
PAA	530.70	396.15	313.47	269.20	34.42	—	5.31	138.73	308.44
C60-PAA (0.78%)	465.35	373.05	294.23	257.65	24.35	—	2.68	142.35	287.97
C60-PAA (1.45%)	482.78	380.76	301.73	267.28	24.23	—	1.06	142.49	299.36
C60-PAA (4.34%)	482.67	346.20	294.22	255.72	23.56	—	0.88	137.89	290.86
									479.73
									576.81



**Figure 6.** (a) DSC spectrum of pure C60; (b) DSC spectrum of PAA; (c) DSC spectrum of C60-PAA (0.78%); (d) DSC spectrum of C60-PAA (1.45%); and (e) DSC spectrum of C60-PAA (4.34%).

**Table III.** DSC profiles of PAA and C60-PAA

Polymer	[ $\Delta H(\text{J/g}/^\circ\text{C})$ ]		Inference
	Exo ( $^\circ\text{C}$ )	Endo ( $^\circ\text{C}$ )	
Pure C60		—	
PAA	183.02	[65.62/182.79]	$T_g$
	255.29		$T_m$
C60-PAA	194.55	[65.16/191.60]	$T_g$
(0.78%)	243.80	[226.7/239.14]	$T_m$
C60-PAA	166.75	[84.67/164.92]	$T_g$
(1.45%)	256.63	[249.7/218.66]	$T_m$
C60-PAA	78.82	[1.242/ 77.13]	$T_{g1}$
(4.34%)	137.84	[38.60/126.19]	$T_{g2}$
	255.16		$T_m$

**Figure 7.** (a) C60-PAA (1.31%); (b) C60-PAA (2.80%); and (c) C60-PAA (4.43%).

heterogeneous morphology. Even 1.31% impregnation of C60 in the polymer enhanced homogeneity but an increase in the percentage of impregnation of C60 into the polymers enhanced heterogeneous morphology. In general, C60-PAA (6.69%) has shown higher heterogeneous character than C60-PAA (4.43%) (Figures 7(a)–(c)).<sup>[24]</sup>

## CONCLUSIONS

Polyacrylic acid (PAA)-C60 copolymers were synthesized through 2,2-azobisisobutyronitrile-initiated in situ polymerization of PAA under a series of reaction conditions in scCO<sub>2</sub>. Polymerization of AA in C60 resulted in an increase in rheoviscosity with concentration of AIBN and temperature under the applied supercritical conditions. The presence of C60 in PAA was ascertained through FT-IR, LIBS, and UV-vis spectra and scanning electron microscopy. UV-vis spectra indicate the formation of C60-PAA as star structure.

The TG-DTA-DSC data show that C60-PAA polymers have improved thermal stability at higher temperature with respect to PAA. Char yield decreases with increasing percentage of C60 content in polymers.

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