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One-Pot Synthesis of a Novel Water-Soluble Fullerene-Core Starlike Macromolecule via Successive Michael and Nucleophilic Addition Reaction

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Successive Michael and nucleophilic addition reaction of an α,β-unsaturated ester (*n*-butyl acrylate) with fullerenol in one pot leading to the formation of a novel water-soluble hydroxy ether terminated fullerene-core starlike macromolecule was classically demonstrated for the first time in fullerene chemistry. FTIR, UV−vis, and TGA techniques were employed for characterization. The chemical attachment of acrylate units to the fullerene core was clearly indicated from the disappearance of typical FTIR peaks of fullerenol (at 1593.2, 1381.2, and 1068 cm^{-1}) in the product. 1,2-Michael addition followed by nucleophilic addition reaction to the carbonyl group in acid-catalyzed reaction was monitored by the disappearance of typical alkene and carbonyl FTIR peaks of the parent acrylate and the appearance of alkane C−H stretching peaks (2964 cm^{-1}) and hydroxy peak (3426 cm^{-1}) in the product. The appearance of two absorption bands in the UV region, coupled with IR and TGA data, strongly indicate the formation of 1,4-Michael addition product in the case of base-catalyzed reaction. The attachment of about 3−4 acrylate units per fullerene core was determined by both gravimetric and thermogravimetric methods. Optical properties and thermal behavior of the products were shown to be influenced by the presence of fullerene.

Introduction

During the past decade several approaches have been made to combine the unique properties of [60]fullerene[1−10] with the specific properties of polymers to obtain an easily processable C_{60}-based thin film polymeric material[11−15] with an outstanding combination of the properties of both materials. Addition of [60]fullerene also considerably modifies the physical and chemical properties of the polymeric materials. Attempts to chemically attach starlike polymers[16−25] and dendritic macromolecules,[26−28] due to the globular three-dimensional structure of the polymeric fragment, may lead to conducting fullerene encapsulated by insulating polymer layers, and also the formation of monofunctional, monodisperse materials of known molecular mass. Utilization of functionalized [60]fullerene to conduct such reactions is an interesting area of recent research. Functionalized fullerenes retain many of the main characteristics of pristine fullerene but are easier to dissolve in common

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solvents and more amenable to further studies.[29−35] Such functionalized fullerene materials have been investigated for their potential applications in nonlinear optical absorbers for limiting pulse laser radiation[36,37] and in photoinduced electron-transfer redox systems.[38−41] In addition, the hydrophilic derivatives have shown promise in medicinal chemistry.[10,42,43] The bis(phenethylamino succinate) C_{60} has been reported to act as a competitive inhibitor of HIV protease.[44] Although a large number of reactions have been carried out with mono- and bis-derivatives, very little progress has been made on the multifunctionalized derivatives.[34] The high solubility of [60]fullerenol in water makes it suitable for carrying out such reactions. Few fullerenol-based polymeric materials have been synthesized,[45−47] and the properties of these materials were shown to be significantly influenced by the presence of fullerene moiety. Recently, we synthesized a novel ether-connected heterocyclic epoxy starlike polymer by selective nucleophilic addition reaction of hydroxy groups of fullerenol with carbonyl groups in heterogeneous medium at ambient alkaline condition using tetrabutylammonium hydroxide (TBAH) as phase-transfer catalyst.[48] The thermal properties of this product were significantly influenced by the presence of fullerenol (almost double; i.e., the degradation of the neat epoxy resin starts at 150 °C, whereas the fullerene-core epoxy star macromolecule's degradation starts only after 300 °C).[48] Evaluation of other properties of this material is currently underway. The selective nucleophilic addition reaction of hydroxy groups of fullerenol prompted us to design a double-bond-terminated starlike macromolecule by the reaction of fullerenol with *n*-butyl acrylate, an α,β-unsaturated ester, with an aim to further polymerize/copolymerize the double bond to obtain a fullerene-containing star-polymer. It is interesting to observe that reaction proceeded through in-situ Michael addition, typical for an α,β-unsaturated ester/carbonyl compound, followed by nucleophilic addition to carbonyl groups of the ester to form a novel water-soluble hydroxy-ether-terminated cyclic starlike macromolecule in the presence of acid catalyst. The hydroxy groups of fullerenol act as polynucleophiles, demonstrating the classic example of Michael and nucleophilic addition reaction of an α,β-unsaturated ester in fullerene chemistry which has not been reported so far. An entirely different product was obtained when the same reaction was carried out in the presence of a base. The progress of the reaction and the nature of the products formed have been monitored by FTIR and UV−vis. The number of acrylate units attached per fullerene was determined by gravimetric and thermogravimetric analysis of the product formed. The present article gives an idea about the formation of various Michael addition products and effect of pH on the mode of reaction, which in turn dictates the nature of the products formed. We have discussed also the optical and thermal properties of these materials.

Experimental Section

Materials. [60]Fullerene was obtained from MER Co. (purity > 99.5%). The sample quality was checked by UV/vis absorption and ^{13}C NMR, and was used without further purification. Butyl acrylate, sodium hydroxide, concentrated hydrochloric acid, and tetrabutylammonium hydroxide (TBAH) (all analytical grade, E Merck) were used as received. Methanol and tetrahydrofuran (THF) (all HPLC grade, E Merck) were used as received.

Synthesis of [60]Fullerenol (II). Compound II was prepared by the reaction of [60]fullerene in toluene and aqueous sodium hydroxide at ambient temperature using TBAH as phase transfer catalyst.[49] The structure of the resulting fullerenol was characterized by elemental analysis and various spectroscopic methods (IR and ^{13}C NMR) and consisted of an average of ca. 16 hydroxy groups per fullerene.[50]

Synthesis of Acid-Catalyzed Fullerene-Cored Heterocyclic Hydroxy-Ether Starlike Macromolecules (IV). In a typical experimental condition, *n*-butyl acrylate (2 g, 10 equiv per hydroxy group of fullerene) was added slowly to an aqueous solution of fullerenol (100 mg, 0.1 mmol) dissolved in 5% concentrated HCl acid solution (350 mL). The reaction mixture was then stirred vigorously for 80 h at 50 °C. The clear dark brown solution was cooled to 5 °C and then slowly basified (pH ∼9) by adding aqueous sodium hydroxide at such a rate that the temperature never rose beyond 10 °C during neutralization. The basic solution was then kept at room temperature overnight to precipitate the desired product. The red-brown product, collected by centrifugation from the aqueous solution, was washed several times with a water−methanol mixture to remove salt, alkali, and unreacted acrylate (if any) completely to give (IV) (yield ∼157 mg).

Synthesis of Base-Catalyzed Fullerene-Cored Hydroxy-Ether Starlike Macromolecules (V). A 150-mL THF solution of *n*-butyl acrylate (2 g) was vigorously stirred with 350 mL of aqueous solution of fullerenol (100 mg) containing sodium hydroxide (3 g) and few drops of TBAH at 50 °C. A brown sludge precipitated out at the bottom after 48 h. Removing THF from top, the aqueous sludge was further stirred for 30 h after adding 2 g more sodium hydroxide to complete the reaction. The red-brown product was allowed to precipitate overnight by adding excess of methanol into

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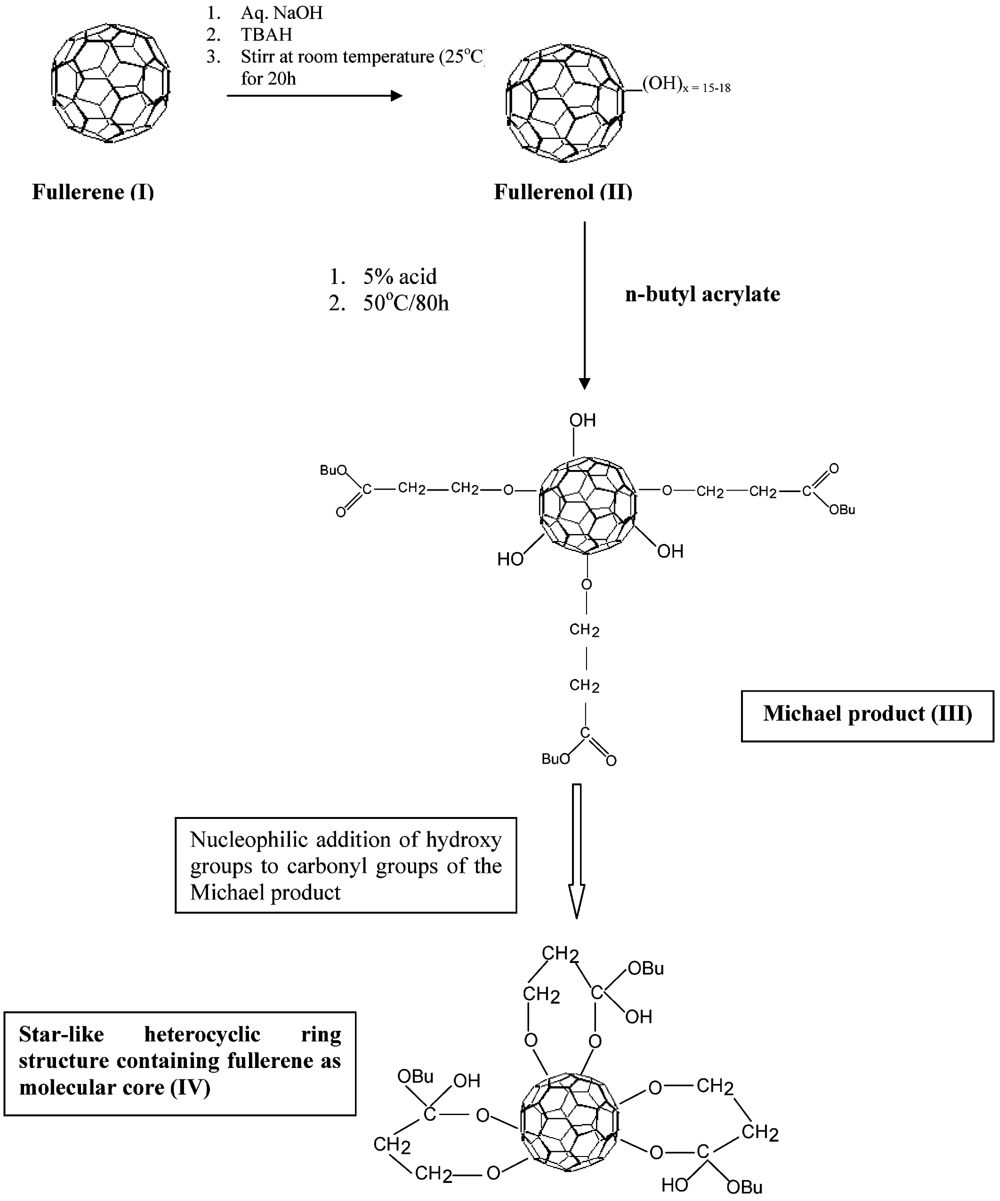
(50) Estimation of the number of hydroxy groups per fullerene in fullerenol by thermal methods. Percentage weight loss due to dehydroxylation of polyols (150−570 °C) = 21; percentage weight loss due to structural degradation of fullerene plus char residue = 57; then number of hydroxy groups per fullerene = (720/57) × (21/17) = 15.6−16; similarly the number of acrylate groups attached to fullerene has been calculated.

Scheme 1. Synthesis of Starlike Heterocyclic Ring Structure Containing Fullerene as Molecular Core by the Reaction of *n*-Butyl Acrylate and Fullerenol in an Acid Medium



the reaction mixture and collected by above method (yield ~143 mg).

Characterization. FT-IR spectra were recorded on a Nicolet Magna IR 750 Spectrometer, using KBr pellets. Thermal properties were measured using a Hi-Res TGA 2950 thermogravimetric analyzer (TA Instruments) attached to a Thermal Analyst 2100 (Du Pont Instruments) thermal analyzer, at a heating rate of 10 °C/min under N_2 atmosphere. The UV–Vis spectra of the products were recorded on a Varian-Cary 500 UV–Vis–NIR spectrophotometer in aqueous solution at equal concentration using redistilled water as the standard reference.

Result and Discussion

Michael and Nucleophilic Addition. The red-brown solid products, obtained by the reaction of fullerenol and *n*-butyl acrylate, are highly soluble in water, and the red-brown solutions are homogeneous and transparent. Structurally, *n*-butyl acrylate is an α,β-unsaturated ester which undergoes 1,2-Michael addition reaction III with fullerenol in the presence of acid. The carbonyl group of the ester then undergoes in-situ nucleophilic addition reaction with another hydroxy group of the same fullerenol with the formation of hydroxy-ether terminated stable seven-member heterocyclic ring structure (**IV**) with starlike shape (Scheme 1). In a similar condition, the base-catalyzed reaction, however, proceeded through 1,4-Michael addition (Scheme 2). The progress of the reaction and the nature of the products formed were monitored by FTIR spectra of fullerenol, alkene, and carbonyl peaks of acrylate. The main bands in the FTIR spectra of unreacted *n*-butyl acrylate [1(A)] and fullerenol [1(B)] occur at 3437, 3075, 3040, 2962, 2874.3, 1935.9, 1727.7, 1637.5, 1620.8, 1464, 1409, 1274.2, 1190.9, 1121.6, 1065.6, 984.4, 910.6, 811.5, 741.1, 668.1, and 506.8 cm^{-1} and 3460, 1543, 1381, and 1068 cm^{-1} respectively, whereas [1(C)] shows the main band FTIR spectra of the reaction product of fullerenol with *n*-butyl acrylate in the presence of acid catalyst at 3426, 2964, 1604, 1406.6, 1262.3, 1096.8, 1023.5, 803, 700, and 445 cm^{-1}, and [1(D)] depicts the main band

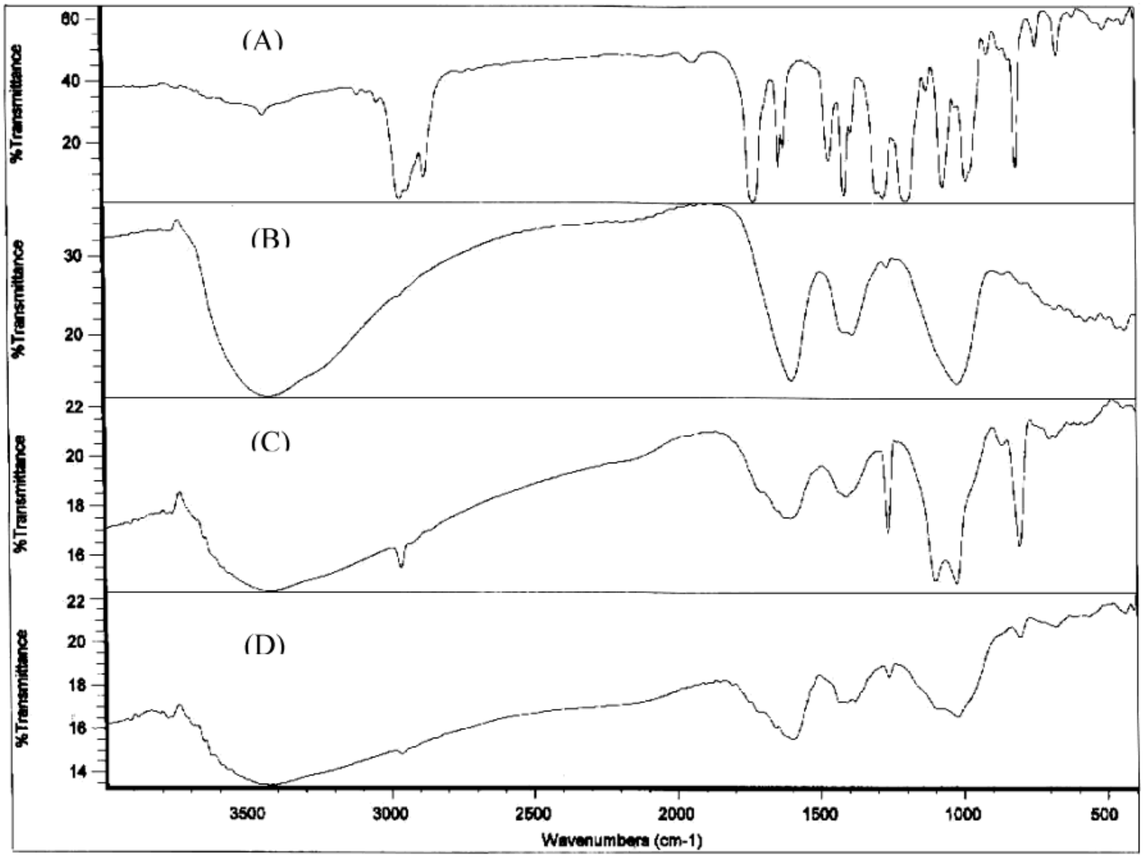
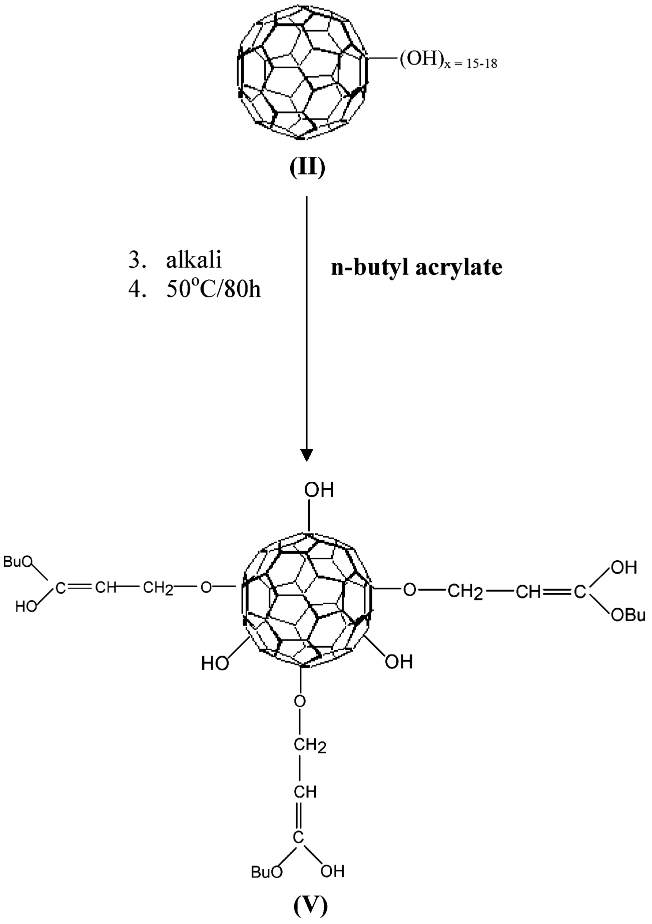


Figure 1. FTIR spectra of the samples: (A) *n*-butyl acrylate, (B) fullerenol, (C) acid-catalyzed product for the reaction of fullerenol with *n*-butyl acrylate, and (D) base-catalyzed product for the reaction of fullerenol with *n*-butyl acrylate.

Scheme 2. Base-Catalyzed 1,4-Michael Addition



FTIR spectra of the reaction product of fullerenol with *n*-butyl acrylate in the presence of base catalyst at 3428, 2964, 1598.6, 1434.5, 1262.3, 1023, 803, 678, 437, and 408 cm^{-1} (Figure 1). Disappearance of the characteristic FTIR peaks of fullerenol [1(B)] at 1593, 1381, and 1068 cm^{-1}, and shifting of the hydroxyl peak of unreacted fullerenol (3460 cm^{-1}), clearly demonstrate that the *n*-butyl acrylate units were chemically attached to the fullerene core which may lead to greater encapsulation. The participation of the double bonds in the formation of Michael addition product was clearly evident from the disappearance of typical alkene bands at 3070, 3040, 1637.5, 1620.8, 1464, 984.4, and 910.6 cm^{-1} in the products (Figure 1(C) and 1(D)). The appearance of C−H stretching band at 2964 cm^{-1} and C−H bending peak at 1406 cm^{-1} in the case of acid-catalyzed product strongly suggest 1,2-Michael addition. Furthermore, the shifting of C−O (str) band from 1274 to 1262.3 cm^{-1} in the product signified that the hydroxy groups of fullerenol act as nucleophile in the Michael addition with the formation of new $C_{60}-O-CH_2$ bond in the product. However, in the case of base-catalyzed reaction, a very weak peak at 2964 cm^{-1} and strong C−H bending peak at 1434 cm^{-1}, give a strong indication for 1,4-Michael addition. Evidently, keto−enol tautomerisms are more favored in acid-catalyzed condition. Further, the UV−Vis spectra and TGA thermograms (discussed later) gave a strong indication for the formation of 1,4-addition product. The disappearance of carbonyl peak (at 1727 cm^{-1}) and shifting of hydroxy peak (from 3460 to 3426 cm^{-1}) in the reaction products suggest nucleophilic addition reaction of hydroxy groups with carbonyl groups of acrylate with the formation of hemiketal (acid-catalyzed) or 1,4-Michael addition (base-catalyzed). Disappearance of carbonyl peaks in the products further suggest that neither hydrolysis nor the transesterification of acrylate could take place during the reaction.

Formation of Ring Structure. Arguably, the position of hydroxy groups taking part in the reaction played a significant role in the nature of the products formed. The reaction of two hydroxy groups of the same fullerenol with the same butyl acrylate will lead to the formation of a stable seven-member cyclic structure, whereas the two hydroxy groups of different fullerenols may result in a highly crowded cross-linked structure. It is well-known that during nucleophilic addition to carbonyl group, the carbonyl carbon changes its hybridization from sp^2 to sp^3 (tetrahedral transition state) and hence the bulky *n*-butyl group attached to carbonyl will be pushed closer to the fullerene moiety, which gives a sterically hindered product. Because the two active sites of the acrylate are separated by only a few atoms, the second reaction path is most unlikely because of the high steric hindrance offered by both fullerene and *n*-butyl group, leaving only the possibility of formation of a starlike cyclic structure.

UV−Visible Analysis. The UV spectra of aqueous solutions of fullerenol and reaction products at the same concentration are depicted in Figure 2. The acrylates are known for their water clarity. The aqueous solutions of the products are homogeneous, transparent, and red-brown colored; intensity increases with increase in the concentration. The UV-spectrum of fullerenol [2(A)] is structureless compared to that of pure [60]fullerene in the visible region,[47] where structured absorption bands of C_{60} are replaced by a steadily decreasing curve, typical for addended C_{60}.[51] The acid-catalyzed product [2(B)] follows the same pattern as that of fullerenol giving strong indication that there is no further attachment of chromophoric (unsaturated) group(s) in the product. The low absorption of acid-catalyzed product compared to that of fullerenol is in full agreement with earlier report.[52] The base-catalyzed product [2(C)], however, shows two absorption bands in the UV region. This gives a strong indication of the presence of some chromophoric group in the product. Considering the single unsaturated group does not absorb in the 200−400 nm region of spectrum ($>C{=}C<$ absorbs at 170 nm), there must be some auxochromic group attached to the chromophore due to which the absorption band shifts to a higher wavelength. The low-intensity absorption at higher wavelength corresponds to $n-\pi^*$ transition, whereas the high-intensity band at lower wavelength corresponds to $\pi-\pi^*$ transition. Coupling this observation with IR data of base-catalyzed product, it can be argued easily that the base-catalyzed reaction follows 1,4-Michael addition with formation of enol, where the hydroxyl group (auxochrome) is directly attached to double bond (chromophore). It is evident from the spectra that the products have high transmittance in the visible region and high absorbance in the UV region, which make them suitable for use in protective lenses or in artificial optical sensors for damage from high-energy laser.

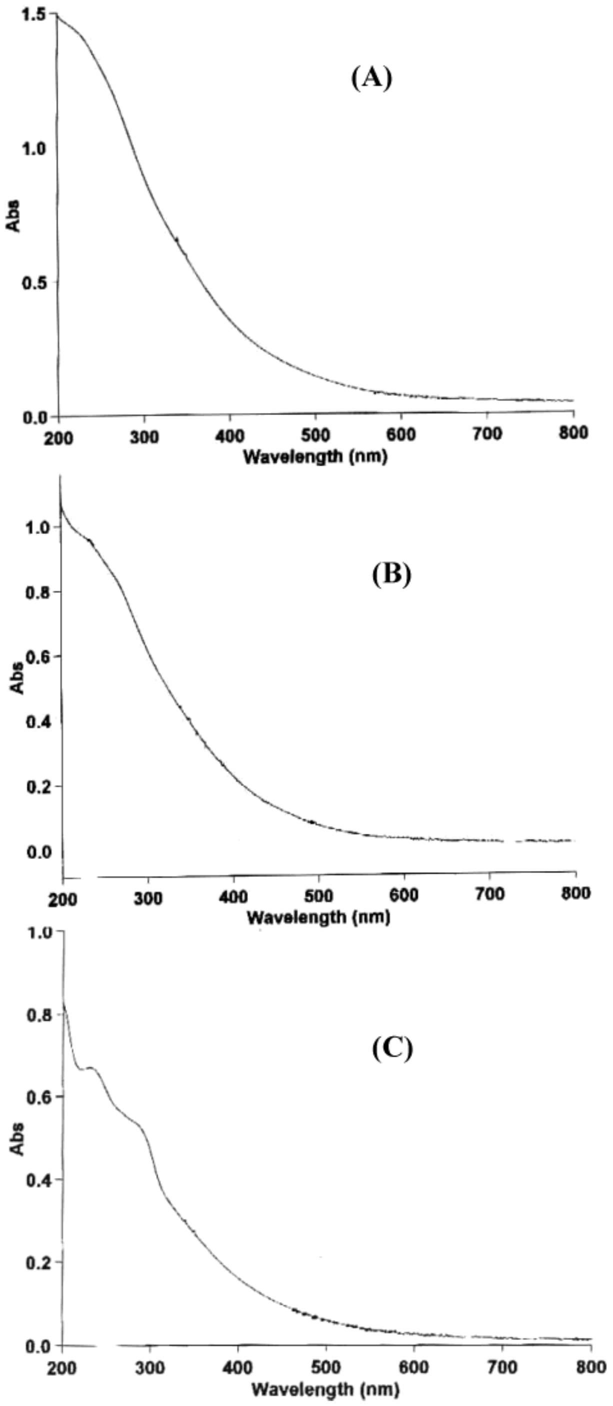


Figure 2. UV−Vis absorption spectra of (A) fullerenol, (B) acid-catalyzed product for the reaction of fullerenol with *n*-butyl acrylate, and (C) base-catalyzed product for the reaction of fullerenol with *n*-butyl acrylate. UV−Vis spectra were measured using redistilled water as the standard reference. All spectra were recorded at the same concentration.

Thermal Behavior. The typical TGA and first-derivative TGA thermograms taken at a heating rate of 10 °C/min in a nitrogen atmosphere of fullerenol and butyl acrylate−fullerenol condensate are depicted in Figure 3. The first-derivative TGA trace of fullerenol [3(A)] offers some interesting observations. There are distinct waves of unequal amplitude at regular intervals on the temperature axis that disappear beyond 275 °C.

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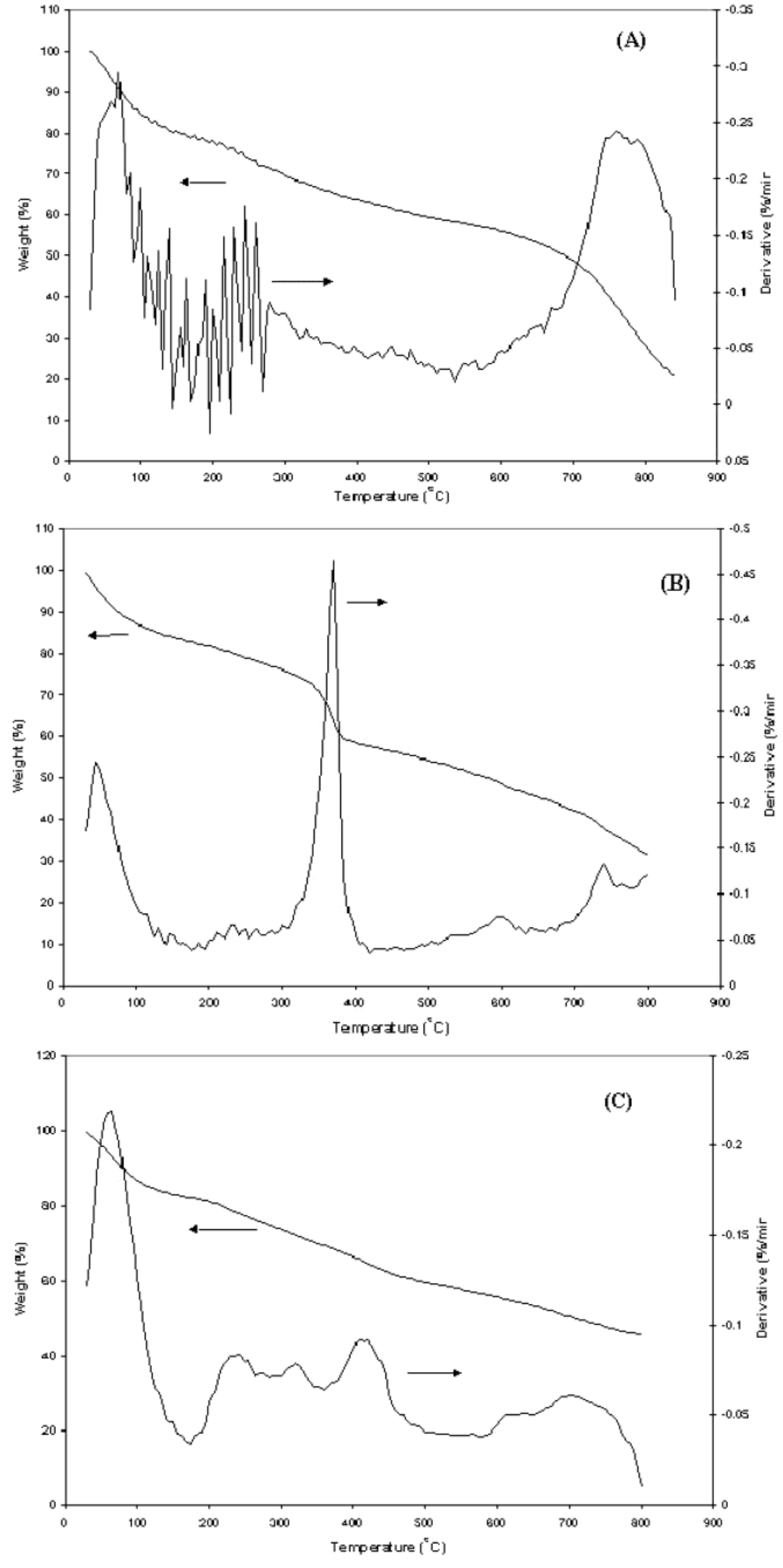

Figure 3. TGA profiles of the samples: (A) fullerenol, (B) acid-catalyzed product for the reaction of fullerenol with *n*-butyl acrylate, and (C) base-catalyzed product for the reaction of fullerenol with *n*-butyl acrylate, obtained in nitrogen atmosphere at a heating rate of 10 °C/min.

A plausible explanation for this observation is that there is a gradual variation in the strength of C_{60}−OH bonds, the strength increasing with decreasing hydroxyl level requires higher temperature for dehydroxylation. The

TGA trace of fullerenol shows a weight loss to the extent of above 21% between the temperature range 150−570 °C. Assuming that there is no adventitious moisture, and degradation occurs only by dehydroxylations, the above weight loss corresponds to about 16 −OH groups per buckyball, consistent with our reported value of 15−18 OH groups.[50]

Acid-catalyzed butyl acrylate−fullerenol condensate [3(B)] follows a thermal pattern similar to that of epoxy−fullerenol condensate[48] and signifies a similar type heterocyclic ring structure in both the cases. Also, the first-derivative TGA trace of the product is particularly unique in the sense that, unlike fullerenol, there is no impression of stepwise dehydroxylation in the lower temperature range. Instead, there is a monotonic weight loss between 150 and 280 °C and then a sharp degradation step between 280 and 410 °C (crest temperature 370 °C) due to degradation of C_{60}-hemiketal groups in distinct steps, identifiable as short but sharp spikes superimposed over the Gaussian peak. Evidently, the C_{60}−hemiketal bond is much stronger than C_{60}−OH bonds, which is responsible for the observed greater thermal stability of the product. The above results give sufficient indication for the hydroxy groups participation in the reaction and encapsulation of fullerene by acrylate unit. The TGA trace of the acid-catalyzed product shows a weight loss to the extent of about 40% (21% in case of fullerenol) between 150 and 570 °C, which corresponds to about four acrylate units per fullerene.[50] Several interesting distinct differences can be observed when base-catalyzed butyl acrylate−fullerenol condensate [3(C)] is compared with acid-catalyzed product. The first-derivative TGA trace of base-catalyzed product shows three distinct stages of degradation in the temperature range 175−430 °C with crest temperatures at 238, 319, and 415 °C. No distinct weight loss step was observed between 280 and 415 °C, and the total weight loss was calculated to be 36% between 150 and 570 °C which corresponds to three acrylate units per fullerene.[50] Possibly first-stage degradation was due to dehydroxylation of polyols still remaining in the product and the third stage was due to the degradation of −OH group of enol. The higher degradation temperature of −OH groups of enol compare to that of hemiketal −OH (about 45 °C) was due to the resonance stabilization of −OH groups of enol. Thus, the thermal behavior of both acid- and base-catalyzed product gave ample evidence for the chemical attachment of acrylate units to fullerene, and the percentage weight loss gave the number of acrylate units attached per fullerene. The higher char yield of the product compared to fullerenol reveals better thermal stability.

Conclusion

The occurrence of typical Michael addition reactions in the case of an α,*β*-unsaturated ester (*n*-butyl acrylate) has been demonstrated for the first time in fullerene chemistry where the hydroxyl groups of [60]fullerenol act as nucleophile. Interestingly, the results show that the base-catalyzed reaction leads only to the formation of 1,4-Michael addition product, whereas the acid-catalyzed reaction not only follows the 1,2-Michael addition but also subsequently follows nucleophilic addition reaction on the carbonyl group with the formation of a cyclic ring structure. Thus, it has been established that the nature of the catalyst plays a significant role in deciding the course of reaction.

The present finding may open up an alternative approach for the synthesis of various fullerene-containing polymeric materials. Thus, [60]fullerene-core nitrile-terminated versatile starlike intermediates can be obtained by Michael addition reaction of acrylonitrile with [60]fullerenol which itself can act as an interesting core to perform Vogtle type dendrimer synthesis or may be suitably functionalized to obtain various ester linked dendrimers or starlike polymers.

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