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# Acid catalyzed 1, 2 Michael addition reaction: a viable synthetic route in designing fullerene core starlike macromolecule

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The paper describes a comprehensive investigation to establish the heterophase acid-catalyzed 1, 2 Michael addition reaction between fullerol (nucleophile) and substituted acrylates ( $R = H, CH_3, Ph$ )/vinyl acrylates (electron deficient olefins). The main emphasis is to evaluate structure–property relationship and establish a mechanism for tuning the structure in different operating conditions, which could be useful while adapting this reaction in designing of fullerene core starlike macromolecules. The effect of substituents on the rate of formation of the product is another important aspect covered in the present paper. The most significant outcome of the present investigation are (i) the nature of the product formed has direct bearing with operating process, whereas, (ii) rate of reaction and the properties of the end-products depends on the nature and position of substituents attached to olefins. Adopting heterogeneous phase reaction scheme, the reaction can be easily controlled at 1, 2 Michael addition stage which otherwise proceeds further to provide cyclic product in single-phase reaction. The nature of the substituent at  $\beta$ -carbon of the olefins have the inverse effect on the rate of the reaction. The steric rather than electronic effect of substituents governs the rate of reaction. However, the significant influence of  $\beta$ -substituents on the properties of the Michael addition products are observed in a more classical manner. The phenyl substituent at the  $\beta$ -position measured the slowest rate of reaction but imparts highest thermal stability. In such systems, the vinyl substitution on esteric carbon further reduces both the reaction rate and the thermal stability. Copyright © 2008 John Wiley & Sons, Ltd. Supplementary electronic material for this paper is available in Wiley InterScience at <http://www.mrw.interscience.wiley.com/suppmat/0894-3230/suppmat/>

**Keywords:** 1; 2 Michael addition reaction; acrylate derivatives of fullerol; fullerene core starlike macromolecule; thermal behaviour; substituent effect

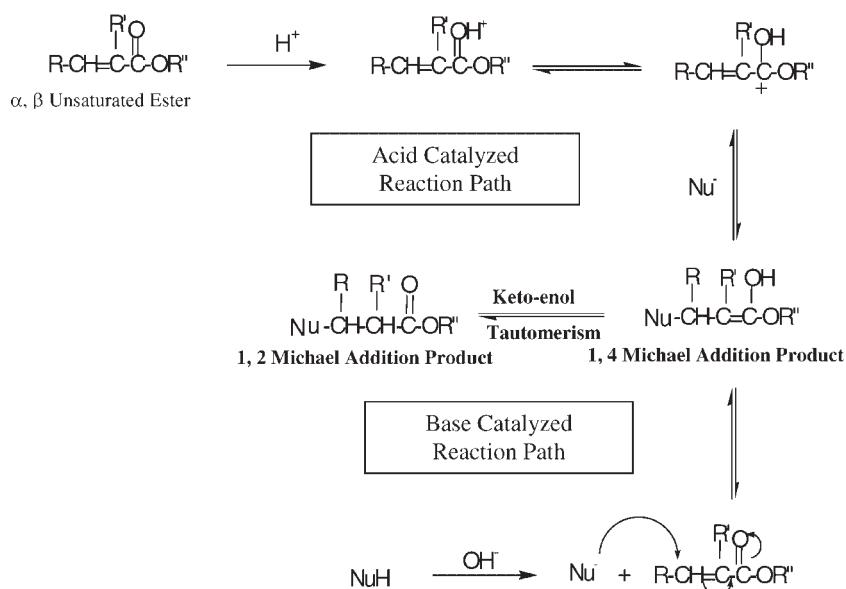
## INTRODUCTION

The conjugative addition of nucleophiles to electron-deficient alkenes is an important synthetic method with wide applications in organic chemistry.<sup>[1]</sup> Addition reaction of active methylene compounds to  $\alpha$ ,  $\beta$ -unsaturated carbonyl compounds in presence of an acid or base is known as Michael addition reaction.<sup>[2]</sup> Mechanistically, the acid and base catalyzed Michael addition reactions proceed in two different path ways following sequence of steps (Scheme 1). Although the Michael addition originates from addition of an active methylene compound to  $\alpha$ ,  $\beta$ -unsaturated carbonyl compound, the domain has now being widened to include  $\alpha$ ,  $\beta$ -unsaturated sulfones,<sup>[3]</sup> nitriles and the other activated double bonds.<sup>[4]</sup> Several hetero-atom nucleophiles<sup>[5]</sup> (alkoxy, cyano, amines etc.) are also being used. Thus, not only for the synthesis of carbon–carbon bond, the Michael addition can be used in carbon–hetero atom bond forming reaction simply by selecting heteroatom nucleophiles. Although these addition reactions are normally carried out in an organic solvent in the presence of strong base<sup>[6]</sup> or acid,<sup>[7]</sup> the formation of organometallic complexes<sup>[5(c)]</sup> and the solvent-free,<sup>[9]</sup> catalyst-free Michael type addition of amines to electron-deficient alkenes are also reported.<sup>[10]</sup> The recent past also records the selection of more innovative reagents and reaction conditions to endorse real versatility in the Michael addition reactions.<sup>[11]</sup>

The last decade had observed several interesting synthetic approaches<sup>[12]</sup> to combine the unique properties of [60]fullerene(s) with specific properties of addended materials to obtain an easily processable  $C_{60}$ -based products with an outstanding combination of the properties of both the materials.<sup>[13]</sup> Fullerene core starlike<sup>[14]</sup> and dendritic macromolecules<sup>[15]</sup> got special attention due to globular three-dimensional structure and the formation of monofunctional, monodisperse materials of known molecular mass within molecular dimension range. Functionalized fullerenes retain many of the main characteristics of the pristine fullerene but are easier to dissolve in common organic solvents and more amenable to further studies.<sup>[16]</sup> Many of these potential materials have been investigated for wide range applications; nonlinear optical absorbers for limiting pulse laser radiation,<sup>[17]</sup> photoinduced electron-transfer redox system<sup>[18]</sup> and medicinal chemistry.<sup>[12(i),19]</sup>

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**Scheme 1.** Acid and base catalyzed Michael addition reaction mechanism

In combination with alkylation and condensation, the Michael addition can be used to construct a wide variety of complex molecules from relatively simple starting materials. Only recently, we have explored the Michael addition reaction as a viable synthetic route to obtain interesting water-soluble  $C_{60}$ -based materials.<sup>[20]</sup> The reaction of *n*-butyl acrylate with fullerenol in presence of both acid and base interestingly yielded 1, 4-Michael addition product for the base-catalyzed reaction, whereas the acid-catalyzed reaction proceeds through 1, 2-Michael addition followed by nucleophilic addition onto the carbonyl group to form the cyclic ring structure. High solubility in water together with its easy release of protons due to strong electrophilic character of the fullerene cage (a new family of proton conductors<sup>[21]</sup>) makes fullerenol<sup>[22]</sup> as an excellent nucleophile to carry out these reactions. The generated fulleroxide (fol)<sup>n-</sup> can undergo selective nucleophilic addition reaction on carbonyl carbon<sup>[23]</sup> and help in design of macromolecular materials.<sup>[24]</sup> Besides this, fullerenols have attracted extensive attention because of their promising applications in diverse fields such as solar energy conservation and storage,<sup>[25]</sup> fuel cells,<sup>[26]</sup> piezoelectric<sup>[27]</sup> and medicinal chemistry.<sup>[28]</sup>

In the present work, a comprehensive investigation on the Michael addition reaction has been carried out to throw light on various perspectives and to examine the scope and applicability of this reaction in designing various fullerene core starlike macromolecular materials. The study mainly focuses on the effect of reagents and process parameters which are essential for useful application of this reaction; that is (i) optimum reaction condition(s), (ii) effective concentration and nature of catalyst, (iii) nature and the positional effect of substituents on the rate of reaction and properties of the final product(s) etc. Detail investigation reveals several interesting observations. The proper selection of process parameters precisely controls the nature of the product formed. The controlled acid catalyzed heterogeneous phase reaction thus, avoids the cyclization step to restrict at 1, 2-Michael addition stage only. Rate of reaction and properties of the final products, on the other hand, are influenced by the nature of the substituents at the  $\beta$ -carbon of the electron

deficient olefins. Thus, in spite of strong  $-I$  and resonance effect, phenyl at  $\beta$ -carbon (ethyl and vinyl cinnamate) records slowest reaction rate, whereas the unsubstituted acrylate (methyl methacrylate) shows the highest rate under similar reaction conditions. Methyl (+I effect, ethyl and vinyl crotonate) on the other hand, exhibits an intermediate effect. The vinylic substitution on the esteric carbon further reduces the reaction rate. Also, the thermal and absorption properties of the products are greatly influenced by the substituent.

## RESULTS AND DISCUSSION

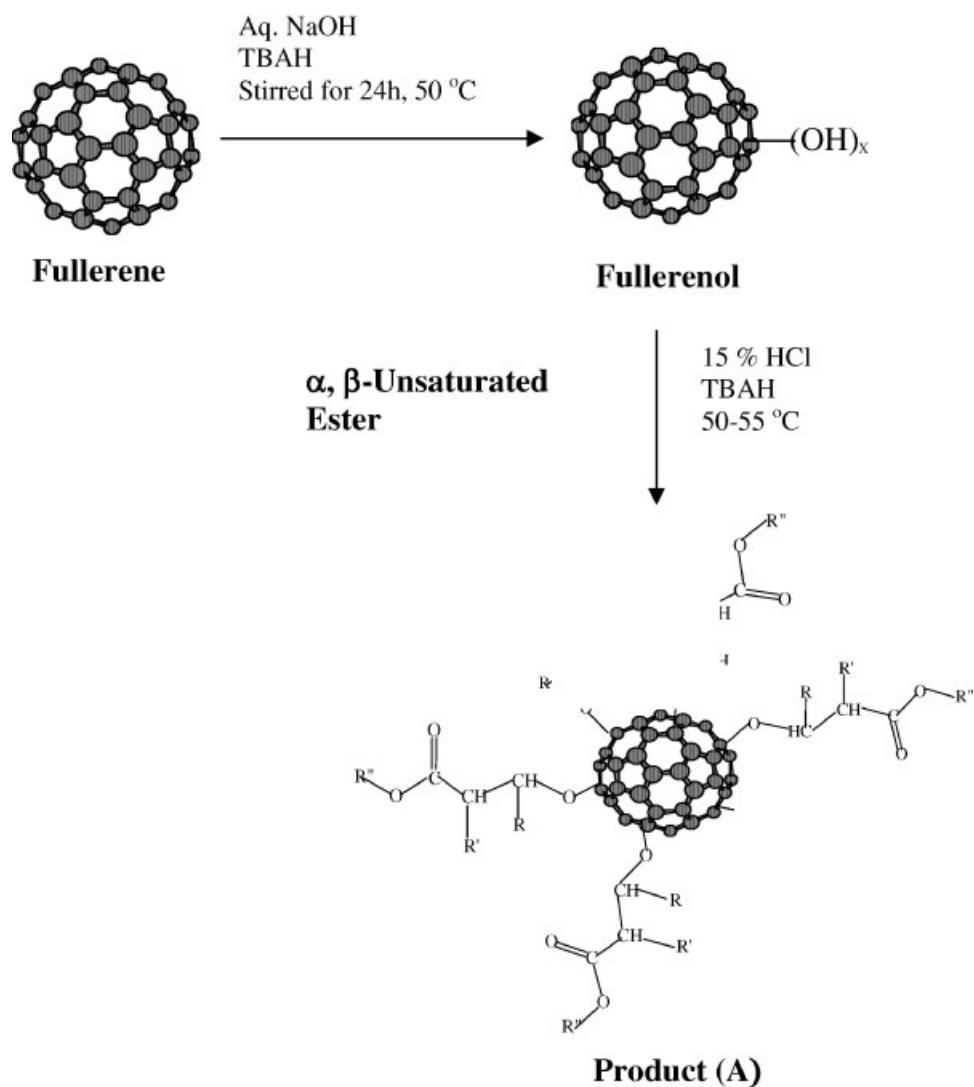
### Synthesis

Scheme 2 represents the Michael addition reaction of acrylates (THF solution) with fullerenol in 15% aqueous HCl solution in presence of tetra butyl ammonium hydroxide (TBAH) as phase transfer catalyst. Table 1 listed the reaction parameters and overall yield. The acrylates (1–5) used and the corresponding Michael addition products (**1a–5a**) are represented in Fig. 1. The following general procedure is adopted for acid-catalyzed Michael addition reaction.

The THF solution of acrylates (1–5) (4 mM in 1 mL THF) was added slowly to a mix aqueous solution of fullerenol (0.02 mM in 10 mL water) and HCl (10 mL 15% aqueous solution) with the addition of 2–3 drops of TBAH. The reaction mixture was stirred vigorously at 50–55°C for the required time (Table 1). Progress of the reaction was monitored by TLC. On completion, the crude red-brown solid product separated out of the reaction medium and collected by centrifugation. Pure products were dried after washing several times with chilled water (to remove the impurity of acid and TBAH) and further washed with ether (to remove the impurity of unreacted ester).

### Identification of products

The acid catalyzed Michael adduct of fullerenol and acrylates are red-brown solid powder (**1a–5a**) soluble in DMSO and methanol/



**Scheme 2.** Synthesis of acid catalyzed 1,2 Michael addition product by the reaction of fullerol with acrylates

water (Table 1). The red-brown solutions are homogeneous and transparent.

The FTIR study not only monitors the chemical attachment of acrylates onto the fullerene core but also identifies their mode of

attachment. The chemical attachment could be ascertained from the disappearance of the typical fullerol peaks at 1593, 1381 and  $1068\text{ cm}^{-1}$  in the FTIR spectra of the products. The general characteristic features of the 1,2 Michael addition reactions

**Table 1.** Reaction parameters and overall yield of acid catalyzed Michael addition reaction between fullerol and substituted acrylates

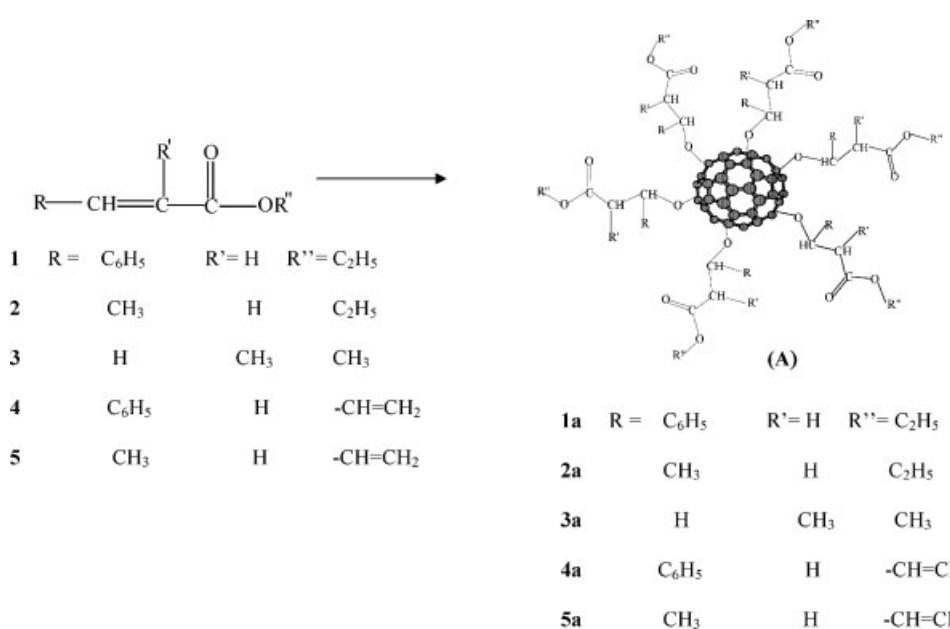
S. no.	Reagent (4 mM)	Catalyst	Temperature (°C)	Time (h)	Product	Solubility*	Yield (mg)
1	1	15% HCl	50–55	32	<b>1a</b>	M	10
2	2	15% HCl	50–55	26	<b>2a</b>	W	10
3	3	15% HCl	50–55	21	<b>3a</b>	M	17
4	4	15% HCl	50–55	42	<b>4a</b>	M	10
5	5	15% HCl	50–55	40	<b>5a</b>	W	11

Fullerenol = 0.02 mM in all cases.

\* All the products are soluble in DMSO.

M = Methanol.

W = Water.



**Figure 1.** Describes the various substituted acrylates/vinyl acrylates used as electron deficient olefins and their corresponding 1, 2 Michael addition product

between acrylates and fullerol are the disappearance of the typical  $\alpha$ ,  $\beta$ -unsaturated double bond peaks of the unreacted acrylates in the products. These alkene peaks generally appear at around  $3020$  ( $\nu$ ,  $=\text{C}-\text{H}$ ),  $1650$  ( $\nu$ ,  $\text{C}=\text{C}$ ) and  $980$  ( $\delta$ ,  $=\text{C}-\text{H}$ )  $\text{cm}^{-1}$ , respectively. On the other hand, the characteristic carbonyl peaks ( $\sim 1740 \text{ cm}^{-1}$ ) and  $\text{C}-\text{O}$  (str) peaks of the ester [i.e.  $-\text{C}(=\text{O})-\text{O}$  at  $\sim 1250$  and  $\text{C}-\text{O}-\text{R}$  ester at  $\sim 1150 \text{ cm}^{-1}$ ] will be retained in the products. In addition, the alcoholic  $\text{C}-\text{O}$  ( $\nu$ )/ $\text{O}-\text{H}$  ( $\delta$ ) peak of fullerol should be shifted in the product due to the formation of new ether (fol-O—C) bond on nucleophilic addition.

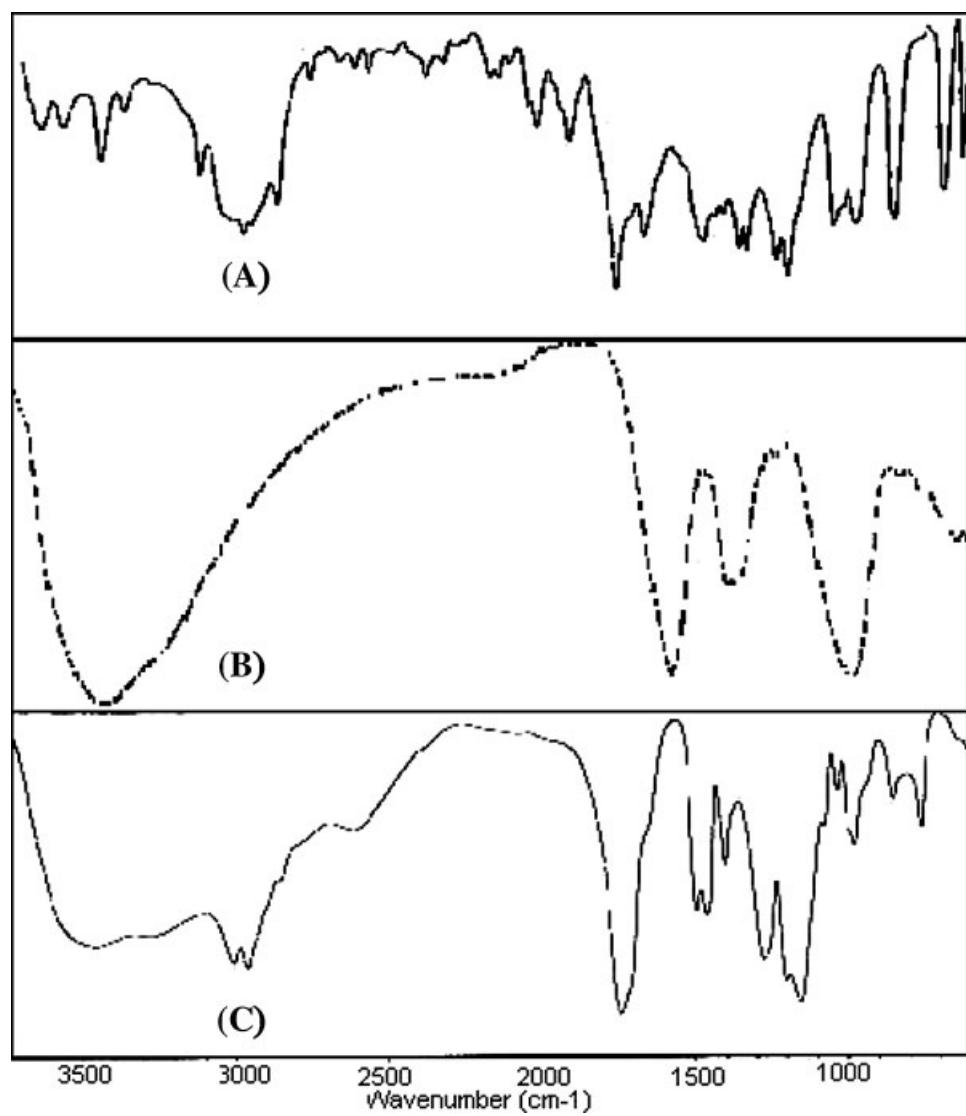
The FTIR spectrum of the acid catalyzed methyl methacrylate reaction with fullerol gives a very clear evidence of 1,2 Michael addition reaction (Fig. 2). The product **3a** retains the carbonyl peak ( $\nu$ ,  $1737 \text{ cm}^{-1}$ ) along with other  $\text{C}-\text{O}$  ( $\nu$ ) peaks of the esters; that is  $\text{C}(=\text{O})-\text{O}$  at  $1271$  and  $\text{C}-\text{O}-\text{CH}_3$  at  $1151 \text{ cm}^{-1}$ , respectively of the unreacted methyl methacrylate (Fig. 2C). At the same time, all the typical peaks of fullerol (2B) and  $\alpha$ ,  $\beta$ -unsaturated double bond peaks of unreacted acrylate (2A) are disappeared in the product. As expected, the alkane  $\text{C}-\text{H}$  ( $\nu$ ) peaks at  $2998$  and  $2954 \text{ cm}^{-1}$  and methyl and methylene bending peaks at  $1484$ ,  $1449$ ,  $1389$  and  $754 \text{ cm}^{-1}$  exist in the product. Similarly, the  $\text{C}-\text{O}$  ( $\nu$ )/ $\text{O}-\text{H}$  ( $\delta$ ) peak of the fullerol is shifted from  $1068$  to  $1023 \text{ cm}^{-1}$  (lower bond strength is nicely reflected in thermal analysis data) due to the formation of fol-O— $\text{CH}_2$  ether linkage in the product. The situation becomes little complicated for the acrylates having additional aromatic and vinylic substituents. The presence of aromatic and vinylic units partially obscures the actual FTIR results. In such cases, the FTIR spectra will also recognize the aromatic/olefinic peaks in addition to other typical peaks. Thus, the FTIR-spectra of **1a**, **4a** and **5a** show aromatic and/or olefinic peaks at  $3027$  ( $\nu$ ,  $=\text{C}-\text{H}$ ),  $1634$  ( $\nu$ ,  $\text{C}=\text{C}$ ),  $1453$  ( $\nu$ ,  $\text{C}=\text{C}$  aromatic),  $870$ ,  $771$  ( $\delta$ , out of plane aromatic  $\text{C}-\text{H}$ ) and  $686$  ( $\delta$ , out of plane aromatic  $\text{C}=\text{C}$ )  $\text{cm}^{-1}$  for **1a** and  $3085$  ( $\nu$ , aromatic  $\text{C}-\text{H}$ ),  $3060$  ( $\nu$ ,  $=\text{C}-\text{H}$ ),  $1632$  ( $\nu$ ,  $\text{C}=\text{C}$ ) and  $860$  ( $\delta$ , out of plane vinylic  $\text{C}-\text{H}$ )  $\text{cm}^{-1}$  for **4a** whereas

product **5a** shows peak at  $1641$  ( $\nu$ ,  $\text{C}=\text{C}$ )  $\text{cm}^{-1}$ , respectively (supporting information<sup>1</sup>).

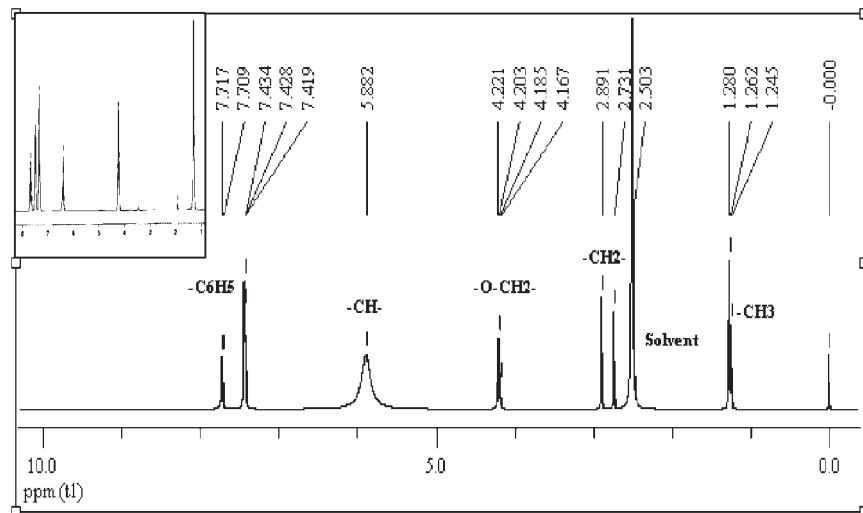
These apparent anomalies in FTIR results can be easily resolved out on analyzing the  $^1\text{H}$  NMR spectra of the corresponding products. The noticeable difference in the chemical shift value and splitting pattern of  $\alpha$ ,  $\beta$ -protons of unreacted acrylates to that of the addended acrylate units on fullerol in  $^1\text{H}$  NMR (due to the lifting of  $\alpha$ ,  $\beta$ -double bond) give a clear view for the structure of the products. In addition, the NMR can easily distinguish the aromatic and olefinic protons as well as the olefinic protons of the acrylic and vinylic units.

The  $^1\text{H}$  NMR spectra of ethyl cinnamate in unreacted form and as Michael adduct are depicted in Fig. 3. The typical  $^1\text{H}$  NMR spectrum of the unreacted ethyl cinnamate (inset) shows peaks at  $\delta$   $1.3$  (t,  $3\text{H}$ ,  $\text{CH}_3$ ),  $4.19$  (q,  $2\text{H}$ ,  $\text{OCH}_2$ ),  $6.39$  (d,  $1\text{H}$ ,  $=\text{CH}-\text{C}(=\text{O})$ ),  $7.3$ – $7.2$  (m,  $5\text{H}$ , aromatic) and  $7.64$  (d,  $1\text{H}$ ,  $=\text{CH}-\text{Ph}$ ), respectively. The peak position of  $\alpha$ ,  $\beta$ -unsaturated double bond protons of the unreacted cinnamate are shifted significantly in the functionalized fullerene (**1a**) due to the saturation of the double bond (Fig. 3). Thus,  $=\text{CH}-\text{C}(=\text{O})$  ( $\alpha$ -protons) peak at  $6.39 \text{ ppm}$  is shifted to  $2.8$ – $2.7 \text{ ppm}$  (d,  $2\text{H}$ ,  $-\text{C}(=\text{O})-\text{CH}_2$ ) and the  $=\text{CH}-\text{Ph}$  ( $\beta$ -proton) at  $7.64 \text{ ppm}$  is shifted to  $5.8 \text{ ppm}$  (b,  $1\text{H}$ ,  $-\text{CH}-\text{Ph}$ ), respectively. The other proton peaks of the unreacted cinnamate do not show any appreciable chemical shift in the functionalized fullerene also. Thus, the methyl and methylene peaks of ethyl ester units appear at  $1.24$  (t,  $3\text{H}$ ,  $-\text{CH}_3$ ) and  $4.16$  (q,  $-2\text{H}$ ,  $\text{O}-\text{CH}_2$ ) respectively. The aromatic peaks also appear as multiplets in the region of  $7.5$ – $7.7 \text{ ppm}$ . The significant upfield shifting of  $\alpha$ - and  $\beta$ - protons in the functionalized fullerene definitely suggests the saturation of the double bond due to 1, 2 Michael addition reaction. The presence of aromatic proton peaks in NMR spectrum also helps in verifying the  $\text{C}=\text{C}$  and  $\text{C}=\text{C}-\text{H}$

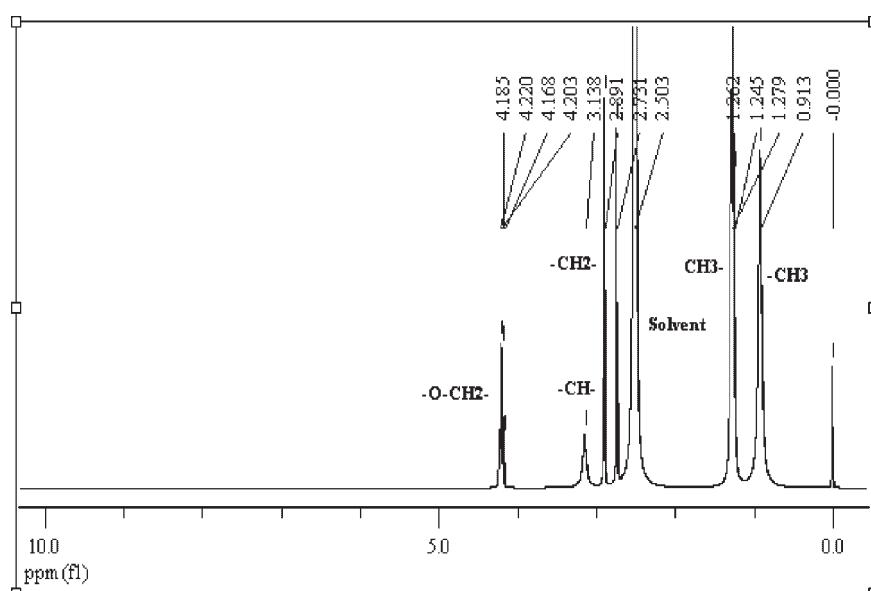
<sup>1</sup>It includes FTIR of **1a**, **4a**, **5a**; <sup>1</sup>H NMR of **3a**, **4a**, **5a**; ESI-MS spectra of **1a**, **2a**, **4a**, **5a**; UV-vis spectra of **2a**, **3a**, **5a** and TGA thermogram and first derivative TGA trace of **1a**, **3a**, **4a**, **5a**.



**Figure 2.** A comparative FTIR spectra of (A) Methyl methacrylate (B) Fullerenol and (C) 1, 2 Michael addition product of methyl methacrylate with fullerenol (**3a**) showing the disappearance of typical double bond peaks and retains ester peaks of the acrylates. Fullerenol peaks have also disappeared



**Figure 3.**  $^1\text{H}$  NMR spectra of ethyl cinnamate 1, 2 Michael addition product (**1a**) describing upfield shifting of  $\alpha$ ,  $\beta$ -proton peaks. Aromatic proton peaks are also observed. Inset showing the proton NMR of pure ethyl cinnamate



**Figure 4.**  $^1\text{H}$  NMR spectra of ethyl crotonate 1,2 Michael addition product (**2a**) presenting two methyl peaks and upfield shifting of  $\alpha$ ,  $\beta$ -proton peaks

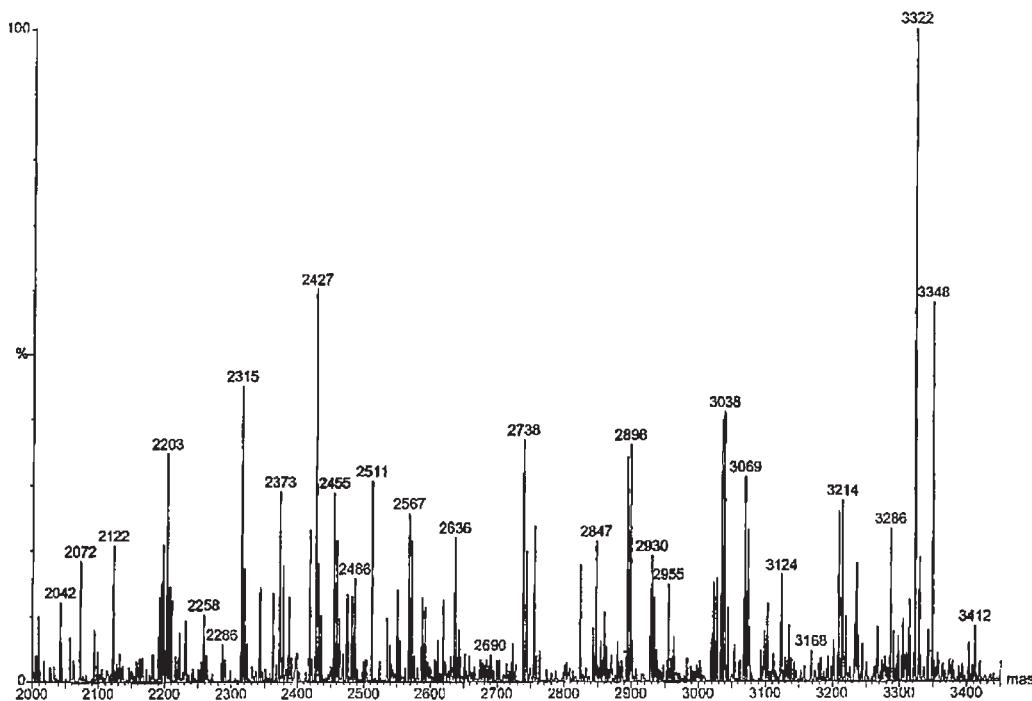
stretchings/bending peaks appearing in FTIR spectra due to phenyl ring. A more clear evidence of 1,2 Michael addition can be observed from the  $^1\text{H}$  NMR spectra of Michael addition product of ethyl crotonate (**2a**, Fig. 4) where the resulting compound does not have either aromatic or olefinic protons and the  $\alpha$ ,  $\beta$ -protons have substantial upfield value compared to unreacted acrylates. The methyl (esteric and  $\beta$ ) groups could also be easily assigned from their distinct chemical shift value and splitting pattern.

ESI-MS of the fullerol-acrylate adducts have been recorded either in methanol or water and the observed molecular ion peak clearly indicates the attachment of variable number of addends.

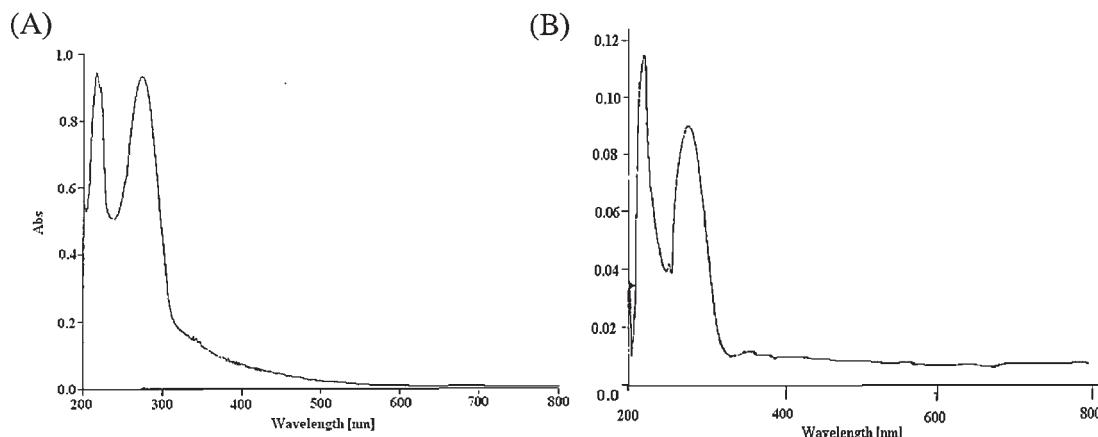
Representative ESI-MS spectrum of **3a** recorded in methanol is shown in Fig. 5. Molecular ion ( $\text{M}^+$ ) peak at  $m/z$  3412 indicates the attachment of 22 methyl methacrylate units (mass of MMA unit = 117) onto a single fullerene core along with 7 unreacted hydroxyl groups. This is the highest observable addended units among the Michael adducts.

#### Absorption properties

The UV-vis spectra of acrylates (1–5) and corresponding Michael addition products (**1a–5a**) are recorded at ambient temperature



**Figure 5.** ESI-MS spectra of methyl methacrylate-fullerenol adduct (**3a**) in methanol.



**Figure 6.** UV-vis spectra of 1, 2 Michael addition products, (A) **1a**, (B) **4a** recorded in methanol showing structured absorption bands in UV region and extended tailing in the entire visible region

(25°C) either in methanol or in water at equal concentration. The unreacted acrylates are transparent, colourless liquid and do not show any significant absorption bands beyond 200 nm except for cinnamates (1 and 4) which show three absorption bands at 204, 216 and 276 nm due to  $\pi-\pi^*$  transition of the aromatic ring. The Michael addition products also show a similar absorption spectral profile but at higher wavelength compared to that of unreacted acrylates and the short tailing of the unreacted acrylates have been extended to the entire visible region due to the presence of fullerene.<sup>[29]</sup> Thus, all other derivatives (**2a**, **3a** and **5a**) do not show any absorption peak except ethyl and vinyl cinnamate (**1a**, **4a** Fig. 6) derivatives that show absorption at 218, 227, 274 and 218, 254, 281 nm, respectively. The steric and  $\pi-\pi$  repulsion between aromatic ring and fullerene and/or vinylic double bond possibly push the absorption bands of aromatic ring slightly towards higher wavelength (lower energy) in the product compared to unreacted acrylates.

### Thermal properties

TGA thermogram and the first derivative TGA trace of Michael adducts and their comparison with unreacted fullerol<sup>[30]</sup> reveal several interesting observations to ascertain chemical attachment of acrylates and also to study the substituents effect on thermal behaviour of the materials.

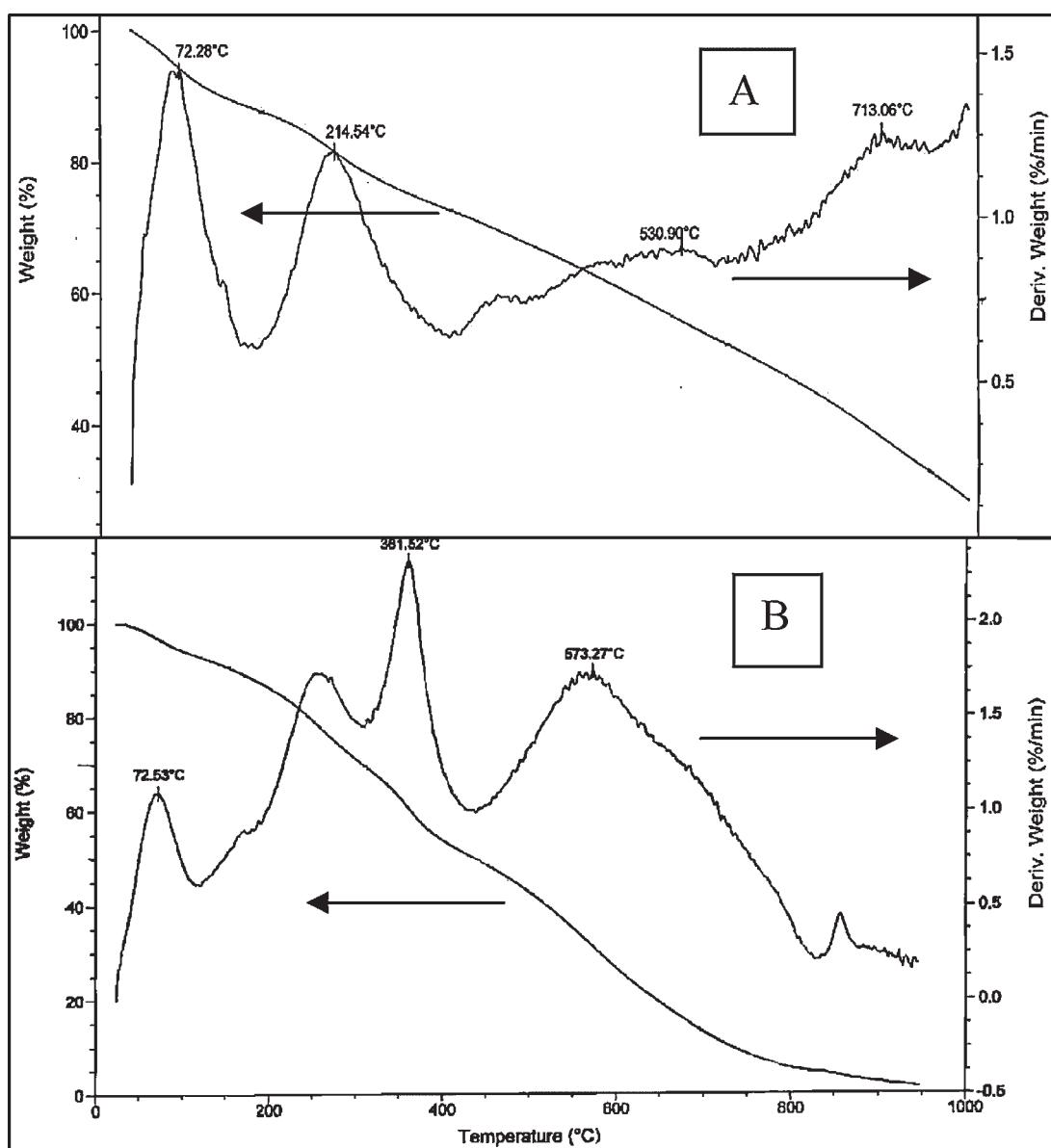
The typical TGA thermograms and first derivative TGA traces of fullerol and Michael adducts taken at a heating rate of 10°C/min in N<sub>2</sub> atmosphere is depicted in Fig. 7 and thermal data are summarized in Table 2. The initial weight loss observed up to 150°C in all the samples was due to the low boiling units inherently present in the samples. The following typical characteristics in thermal features distinguish fullerol from chemically modified fullerol (Michael adducts):

- The first derivative TGA trace of Michael adducts show a distinct step for dehydroxylation at higher temperature (crest temperature appearing around 230–250°C) compared to pristine fullerol (214°C).
- An additional step in first derivative TGA appears at higher temperature (480°C or above) for all Michael adducts which is absent in unreacted fullerol.
- Percentage weight loss due to addends in the temperature range 150–570°C is higher in Michael adducts compared to

unreacted fullerol except for the substituents which show incomplete degradation due to higher bond strength for fol-O-CHPh (**1a** and **4a**).

The above observations clearly suggest chemical attachment of acrylate units onto fullerene core. Chemical attachment of acrylate units encapsulate the remaining hydroxyl groups needing higher temperature for dehydroxylation (230–250°C) of the residual hydroxyl groups compared to the free hydroxyl groups. The additional degradation step at higher temperature for Michael adducts is solely due to the contribution of acrylate units attached to fullerol. The variable bond strength of Fol-O—CH<sub>2</sub> in Michael adducts and the associated degradation of the acrylate units are clearly identifiable as short but sharp spikes superimposed over the Gaussian curve at higher temperature. The increased formula weight (FW) of acrylate units compared to hydroxyl groups expectedly and correctly reflects the higher percentage weight loss due to addends in Michael adducts.

Several interesting differences are also observed in thermal behaviour among Michael adducts (Fig. 8). Except methyl methacrylate, which shows a clear stage of degradation, all the other Michael adducts show monotonic weight loss in TGA thermogram similar to that of fullerol. Similarly, all Michael adducts show two step degradations (supporting information) in the first derivative TGA trace except **2a** which shows three steps degradation. It has also been observed that **3a** shows an abnormally high weight loss within narrow temperature range (~72% between 250–450°C) whereas, **1a** and **4a** show incomplete degradation up to 570°C (~36 and 42% respectively). The wide variation of crest temperature range (480–590°C) for degradation of attached acrylate describes the variable thermal behaviour due to substituents and bond strength for Fol-O—CHR— (R = H, Ph and CH<sub>3</sub>). It is apparent from the thermal data that the absence of substituents at the  $\beta$ -carbon drastically reduces the thermal stability of **3a** whereas the presence of phenyl group at the  $\beta$ -carbon atom significantly improve the thermal stability of **1a** and **4a**. Methyl substituent at  $\beta$ -carbon has a moderate thermal effect (**2a** and **5a**). Interestingly, the heterogeneous phase acid-catalyzed Michael addition products follow the similar degradation pattern but peaks are at different temperature range compared to that of heterogeneous phase base-catalyzed addition product.<sup>[20]</sup> The crest



**Figure 7.** A representative TGA thermogram and first derivative TGA trace of (A) Fullerol, (B) **2a** show single degradation step for fullerol (crest temp 214.5°C) and three stage degradation for **2a** between the temperature range 150–570°C

**Table 2.** Temperature range for thermal degradation and % weight loss of Michael addition products recorded in N<sub>2</sub>-atm at a heating rate of 10°C/min

S. no.	Product	Degradation		
		Temp range (°C)	%wt loss	Crest temp (°C)
1	Fullerol	150–570	36	214.5
2	1a	150–570	36.8	229.8, 543.7
3	2a	150–570	62.4	255.5, 361.5, 573.2
4	3a	150–570	84	232.7, 422.0
5	4a	150–570	42.4	246.8, 589.0
6	5a	150–570	71.2	237.2, 479.0

temperature (in the range of 235–255°C) appearing due to the dehydroxylation of residual polyol in the modified fullerenols are however, very close to each other and easily comparable to base-catalyzed product suggesting similar thermal encapsulation of residual hydroxyl groups in both the cases. The additional degradation step appearing for **2a** (crest temperature 361.5°C) is due to the elimination of esteric  $-\text{O}-\text{C}_2\text{H}_5$  group as a separate step.

#### Process design and steric versus electronic effect

The analyses of the above results help in apprehending the effect of reaction parameters on the nature of the final product(s) and substantial influence of substituents in controlling the rate of reaction and properties of the final products. The retained carbonyl and esteric peaks and disappearance of alkene peaks of acrylates (due to  $\alpha$ ,  $\beta$ -unsaturated double bond) in hetero-

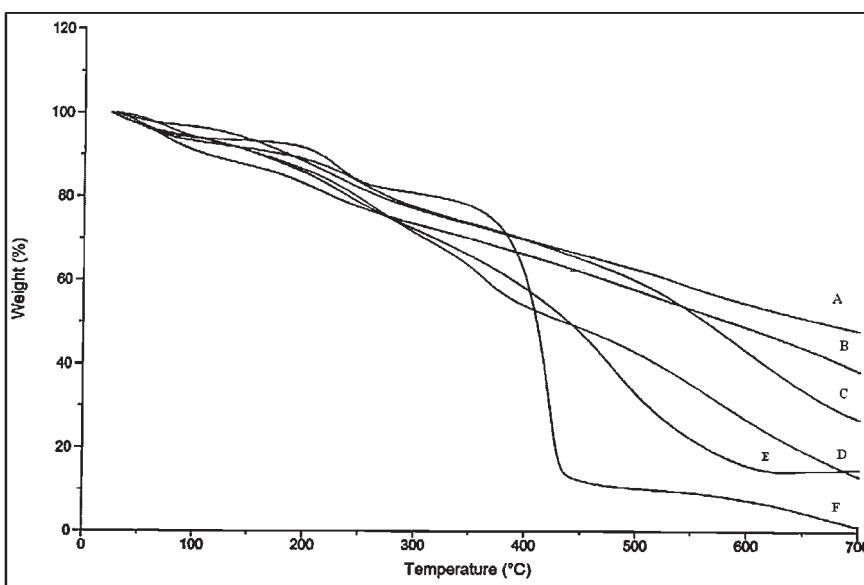


Figure 8. TGA thermogram of (A) **1a**, (B) Fullerenol, (C) **4a**, (D) **2a**, (E) **5a**, (F) **3a** recorded under  $N_2$  atmosphere at the heating rate of  $10^\circ C/min$

geneous phase acid catalyzed reaction easily establish 1, 2-Michael addition reaction. In similar experimental condition, the single-phase acid catalyzed reaction yielded cyclic products<sup>[20]</sup> due to successive 1, 2-Michael addition followed by selective nucleophilic addition reaction to carbonyl carbon<sup>[23]</sup> through vicinal hydroxyl group of fullerenol. The process operation visibly guides the nature of final product. The heterogeneous phase reaction provides better control of the final product and the small alteration of reaction scheme could thus produce two different products with same reagents and reaction parameters.

The steric and electronic effect of the substituents on Michael addition reaction can be evaluated from the acrylates (1–5) selected in the present study. The ethyl cinnamate (1) and crotonate (2) have phenyl and methyl substitution at  $\beta$ -carbon respectively, whereas, the methyl position is shifted to  $\alpha$ -carbon in methyl methacrylate (3). Similarly, vinyl cinnamate (4) and crotonate (5) have vinyl ether group attached to carbonyl carbon (replacing ethyl group) compared to (1) and (2), respectively. Electronically the phenyl has both  $-I$  and strong resonance effect. Methyl, on the other hand, has  $+I$  effect only. The presence of phenyl at  $\beta$ -carbon (1 and 4) is, therefore, expected to increase the electrophilic character (more electron deficient centre) at the  $\beta$ -carbon and should facilitate Michael addition reaction. Inversely, the presence of methyl at  $\beta$ -carbon (2 and 5) should effectively reduce the addition rate. Methyl methacrylate (3) has no substitution at  $\beta$ -carbon; the methyl group is attached to both  $\alpha$ -carbon and esteric oxygen. Interestingly, the experimental results suggest that, contrary to the normal expectation, the acid catalyzed 1, 2 Michael addition proceeds through some unusual manner; slowest in the case of phenyl-substituted acrylates (1 and 4), slower for methyl-substituted acrylates (2 and 5) and fastest with unsubstituted acrylate (3) (Table 1). A plausible explanation may be obtained by comparing the steric versus electronic effect of the  $\beta$ -substituent of the olefins. Although  $-I$  and strong resonance effect of the phenyl group should create more electron deficient centre (more carbonium character) at  $\beta$ -carbon atom to facilitate the Michael addition reaction at faster rate, the bulky phenyl group (1 and 4) at the same time is

expected to have maximum steric effect compared to methyl (2 and 5) and hydrogen (3). The methyl group at  $\beta$ -carbon, on the other hand, have both the unfavoured electronic ( $+I$  effect) and moderate steric effect compared to unsubstituted alkenes. The nucleophile (fol)<sup>n-</sup> also contains bulky fullerene attached in close proximity to hydroxyl group and the steric and  $\pi-\pi$  electronic repulsion between bulky phenyl and fullerene must have hindered the reaction. Predominance of the steric factor over electronic effect is thus clearly visible from the slowest reaction rate for phenyl-substituted acrylates (**1a** and **4a**). On the other hand, although highly unfavoured electronically, the moderate steric effect of methyl (**2a** and **5a**) provide a slightly better rate compared to phenyl but slower compared to unsubstituted acrylates (**3a**). The results also indicate that vinyl ether at esteric carbon (4 and 5) further reduce the reaction rate.

## CONCLUSION

The result demonstrates heterogeneous phase acid-catalyzed 1, 2 Michael addition reaction using fullerenol as nucleophile and substituted acrylates as electron deficient alkenes. The nature of substitution at  $\beta$ -carbon of the electron deficient alkenes has significant influence on the reaction rate. The outcome of the results suggests the predominance of steric-effect over electronic-effect in controlling the reaction. The results also suggest that vinylic unit at esteric carbon causes further slowing of the reaction rate and vinylic double bond remains unperturbed during the course of reaction. The absorption and thermal property of the Michael addition products also have significant influence of substitution. The phenyl substituted Michael adducts exhibits highest thermal stability which is slightly reduced on attaching vinylic units at the esteric position.

Detail investigation thus provides a new viable synthetic route in designing various novel fullerene core starlike macromolecules. The preference for Michael addition of fullerenol creates further opportunities in designing macromolecules having terminal functional groups and will also help to construct Vogtle type dendrimers and polymeric materials. This scheme can be

well extended to study the reaction in base-catalyzed condition and also to examine the other electron deficient alkenes like sulfones, nitriles, carbonyls, amides etc.

## EXPERIMENTAL SECTION

### Materials

[60]Fullerene was obtained from MER Co. (purity > 99.5%). The sample quality was checked by Mass, UV-vis absorption,  $^{13}\text{C}$  NMR, and was used without further purification. Different  $\alpha$ ,  $\beta$ -unsaturated esters, sodium hydroxide, concentrated hydrochloric acid and TBAH (all analytical grade, E Merck/Lancaster/Acros) were used as received. All solvents were purified and dried before use following standard procedure.

### Synthesis of $\text{C}_{60}(\text{OH})_{26-28}$

Fullerenol was prepared by the reaction of [60]fullerene in toluene and aqueous sodium hydroxide at 50°C using TBAH as phase transfer catalyst.<sup>[22]</sup> The structure of the resulting fullerenol was characterized by elemental analysis and various spectroscopic methods (IR,  $^1\text{H}/^{13}\text{C}$  NMR and ESI-MS).

### 1, 2 Michael addition product of ethyl cinnamate (1a)

The THF solution of ethyl cinnamate (1) (4 mM in 1 mL THF) was added slowly to a mix aqueous solution of fullerenol (0.02 mM in 10 mL water) and 15% HCl solution (10 mL) with the addition of few (2–3) drops of TBAH. The reaction mixture was stirred vigorously at 50–55°C for 32 h. The solid product (**1a**) is collected by centrifugation and dried after washing several times with chilled water (to remove the impurity of acid and TBAH) till the aqueous extract becomes neutral. The product was further washed with ether to remove the impurity of unreacted ester (yield = 10 mg). Solubility: DMSO and Methanol. FTIR (KBr,  $\text{cm}^{-1}$ ): 3392 ( $\nu$ , O—H), 3027 ( $\nu$ , =C—H aromatic), 2964, 2872 ( $\nu$ , C—H), 1714 ( $\nu$ , C=O), 1634, 1453 ( $\nu$ , C=C aromatic), 1373, 1313 ( $\delta$ ,  $\text{CH}_3$ ), 1250 ( $\delta$ , (C=O)—O), 1181 ( $\delta$ , C—O—C ester), 1073 ( $\delta$ , C—O—C ether), 870, 771, ( $\delta$ , out of plane aromatic C—H) and 686 ( $\delta$ , out of plane aromatic C=C).  $^1\text{H}$  NMR (DMSO,  $\delta$ ) 1.24 (t, 3H, — $\text{CH}_3$ ), 2.7 and 2.8 (d, 2H, — $\text{CH}_2$ —C=O), 4.16 (q, 2H, —O— $\text{CH}_2$ —), 5.8 (b, 1H, —CH—), 7.4–7.7 (m, 5H, aromatic protons). ESI-MS (% fragment) m/z 3456 ( $\text{C}_{60}$  + 14 units + 2OH), 3422 (5,  $\text{C}_{60}$  + 14 units), 2702 (12,  $\text{C}_{60}$  + 10 units + 3OH), 2298 (10,  $\text{C}_{60}$  + 8 units + 2OH). UV-vis (Methanol, nm) 218, 227 and 274 with extended tailing in the entire visible region.

### 1, 2 Michael addition product of ethyl crotonate (2a)

Synthesis and purification steps followed as above using ethyl crotonate (2) as substrate. Reaction time: 26 h. Yield = 10 mg. Solubility: DMSO and Water. FTIR (KBr,  $\text{cm}^{-1}$ ): 3388 ( $\nu$ , O—H), 2922, 2863 ( $\nu$ , C—H), 1726 ( $\nu$ , C=O), 1458 and 1379 ( $\delta$ ,  $\text{CH}_3$ ), 1256 ( $\delta$ , (C=O)—O), 1178 ( $\delta$ , C—O—C ester), 1068 ( $\delta$ , C—O—C ether), 795, ( $\delta$ ,  $\text{CH}_2$ ).  $^1\text{H}$  NMR (DMSO,  $\delta$ ) 0.91 (b, 3H, — $\text{CH}_3$  on  $\beta$ -carbon), 1.2 (t, 3H, — $\text{CH}_3$ ), 2.7 and 2.8 (d, 2H, — $\text{CH}_2$ —C=O), 3.13 (b, 1H, —CH—), 4.16 (q, 2H, —O— $\text{CH}_2$ —). ESI-MS (% fragment) m/z 2546 (M<sup>+</sup>, 20,  $\text{C}_{60}$  + 13 units), 2462 (25,  $\text{C}_{60}$  + 12 units + 10OH), 2426 (10,  $\text{C}_{60}$  + 12 units + 8OH), 2392 (40,  $\text{C}_{60}$  + 12 units + 6OH), 2342 (20,  $\text{C}_{60}$  + 12 units + 3OH), 2312 (15,  $\text{C}_{60}$  + 11 units + 9OH), 2298 (20,  $\text{C}_{60}$  + 11 units + 8OH), 2282 (100,  $\text{C}_{60}$  + 11 units + 7OH),

2228 (10,  $\text{C}_{60}$  + 11 units + 4OH), 2210 (10,  $\text{C}_{60}$  + 11 units + 3OH), 2186 (20,  $\text{C}_{60}$  + 10 units + 9OH), 2114 (35,  $\text{C}_{60}$  + 10 units + 5OH), 2082 (30,  $\text{C}_{60}$  + 10 units + 3OH), 2002 (10,  $\text{C}_{60}$  + 9 units + 6OH), 1900 (15,  $\text{C}_{60}$  + 9 units), 1834 (10,  $\text{C}_{60}$  + 8 units + 4OH). UV-vis (Water, nm) structureless absorption with extended tailing in the entire visible region.

### 1, 2 Michael addition product of methyl methacrylate (3a)

Synthesized and purified as above using methyl methacrylate (3) as the electron deficient olefine. Reaction time: 21 h. Yield = 17 mg. Solubility: DMSO and Methanol. FTIR (Fig. 2C, KBr,  $\text{cm}^{-1}$ ) 3448 ( $\nu$ , O—H), 2998, 2954 ( $\nu$ , C—H), 1737 ( $\nu$ , C=O), 1484, 1449 and 1389 ( $\delta$ ,  $\text{CH}_3$ ), 1271 ( $\delta$ , (C=O)—O), 1151 ( $\delta$ , C—O—C ester), 1023 ( $\delta$ , C—O—C ether), 754 ( $\delta$ ,  $\text{CH}_2$ ).  $^1\text{H}$  NMR (DMSO,  $\delta$ ) 0.86 (d, 3H,  $\text{CH}_3$  on  $\alpha$ -carbon), 2.7 and 2.8 (d, 2H,  $\beta$ - $\text{CH}_2$ ), 3.16 (1H, —CH—), 3.54 (s, 3H, —O— $\text{CH}_3$ ). ESI-MS (% fragment) m/z 3412 (M<sup>+</sup>, 10,  $\text{C}_{60}$  + 22 units + 7OH), 3348 (60,  $\text{C}_{60}$  + 22 units + 3OH), 3322 (100, 3412-5H<sub>2</sub>O), 2258 (10,  $\text{C}_{60}$  + 13 units + OH), 2122 (20,  $\text{C}_{60}$  + 12 units), 2007 ( $\text{C}_{60}$  + 11 units). UV-vis (Methanol, nm) structureless absorption with extended tailing in entire visible region.

### 1, 2 Michael addition product of vinyl cinnamate (4a)

The procedure adapted for synthesis and purification as mentioned above using vinyl cinnamate (4) as substrate. Reaction time: 42 h. Yield = 10 mg. Solubility: DMSO and Methanol. FTIR (KBr,  $\text{cm}^{-1}$ ) 3380 ( $\nu$ , O—H), 3085 ( $\nu$ , aromatic =C—H), 3060 ( $\nu$ , =C—H), peaks between 2900–2800 ( $\nu$ , C—H), 1723 ( $\nu$ , C=O), 1632 ( $\nu$ , C=C), 1420 and 1384 ( $\delta$ ,  $\text{CH}_3$ ), 1247 ( $\delta$ , (C=O)—O), 1157 ( $\delta$ , C—O—C ester), 1070 ( $\delta$ , C—O—C ether), 860 ( $\delta$ , vinylic C—H out of plane).  $^1\text{H}$  NMR (DMSO,  $\delta$ ) 2.7 and 2.9 (d, 2H, — $\text{CH}_2$ —), 4.2 (b, 1H, —CH—), 6.5–6.6 and 6.7–6.8 (dd, 2H, vinylic = $\text{CH}_2$ ), 7.4 (b, 1H, vinylic —CH=), 7.6–8.0 (m, 5H, Ph). ESI-MS (% fragment) m/z 4102 (10,  $\text{C}_{60}$  + 17 units + 8OH), base peak 3862 (100,  $\text{C}_{60}$  + 16 units + 5OH), 3602 (5,  $\text{C}_{60}$  + 15 units + OH), 3146 (12,  $\text{C}_{60}$  + 12 units + 8OH), 2906 (15,  $\text{C}_{60}$  + 11 units + 5OH), 2474 (5,  $\text{C}_{60}$  + 9 units + 2OH). UV-vis (Methanol, nm) 204, 218, 254 and 281 with extended tailing in the entire visible region.

### 1, 2 Michael addition product of vinyl crotonate (5a)

Synthesized and purified as above using vinyl crotonate (5) as the electron deficient olefine. Reaction time: 40 h. Yield = 11 mg. Solubility in DMSO and water. FTIR (KBr,  $\text{cm}^{-1}$ ) 3377 ( $\nu$ , O—H), peaks between 2900–2800 ( $\nu$ , C—H), 1719 ( $\nu$ , C=O), 1641 ( $\nu$ , C=C), 1428 and 1380 ( $\delta$ ,  $\text{CH}_3$ ), 1247 ( $\delta$ , (C=O)—O), 1068 ( $\delta$ , C—O—C ether).  $^1\text{H}$  NMR (DMSO,  $\delta$ ) 1.23 (b, 3H,  $\text{CH}_3$ ), 2.7 and 2.8 (d, 2H, — $\text{CH}_2$ —), 3.3 (b, 1H, —CH—), 5.3 and 6.6 (two d, 2H, vinylic = $\text{CH}_2$ ), 7.4 (d, 1H, vinylic —CH=). ESI-MS (% fragment) m/z 2660 (M<sup>+</sup>, 60,  $\text{C}_{60}$  + 14 units + 8OH), 2644 (10,  $\text{C}_{60}$  + 14 units + 7OH), 2518 (50,  $\text{C}_{60}$  + 13 units + 7OH), 2432 (25,  $\text{C}_{60}$  + 13 units + 2OH), 2412 (100,  $\text{C}_{60}$  + 13 units + OH), 2304 (5,  $\text{C}_{60}$  + 12 units + 2OH), 2256 (10,  $\text{C}_{60}$  + 11 units + 7OH), 2172 (38,  $\text{C}_{60}$  + 11 units + 2OH), 2158 (10,  $\text{C}_{60}$  + 11 units + OH). UV-vis (Water, nm) structureless absorption with tailing in entire visible region.

### Characterization Techniques

FT-IR spectra were recorded on a Nicolet Magna IR 750 Spectrometer, using KBr pellets.  $^1\text{H}$  NMR spectra were recorded on Bruker Av 400 spectrometer operating at frequency of 400 MHz in DMSO using TMS as the internal standard. The

electrospray mass spectra (ESI-MS) were recorded on a MICROMASS QUATTRO II triple quadrupole mass spectrometer. The sample (dissolved in water/methanol) was introduced into the ESI source through a syringe pump at the rate of 5  $\mu$ L per min. The ESI capillary was set at 3.5 kV and the cone voltage was 20–25 V. The spectra were collected in 6 s scans and the print outs are averaged spectra of 6–8 such scans. The UV-vis spectra of the products were recorded on a Varian-CARY 500 UV-VIS-NIR spectrophotometer in aqueous/methanolic solution at equal concentration. 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<sub>2</sub> atmosphere.

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