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Thermal analysis: a unique method to estimate the number of substituents in fullerene derivatives

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Abstract

Without resorting to any spectroscopic and chromatographic methods, the simple thermal analyses techniques like thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been successfully exploited to calculate the number of groups attached per fullerene unit in various fullerene derivatives. The efficiency of these techniques were tested not only with simple derivatives like fullerenol but also with various fullerene core star-like macromolecular systems. These techniques were found to be independent of nature of the groups attached and products formed. The percentage weight loss in TGA has been exploited to calculate the number of addends on fullerene having definite molecular weight (hydroxyl groups and *n*-butyl acrylate) and enthalpy changes in DSC associated with the dehydroxylation of the unreacted −OH groups have been used as a parameter to calculate the number of addends on fullerene having limited knowledge of molecular weight (polymeric materials like epoxy resins).

Keywords: DSC; TGA; Fullerenol-epoxy star polymer; Fullerenol-acrylate star macromolecule

1. Introduction

During the last decade several approaches have been made to combine unique properties of fullerene [1–10] with the specific properties of the polymers to obtain an easily processable C_{60}-based thin film polymeric material [11–15] with outstanding combination of the properties of both the materials. Addition of fullerene also modifies considerably the physical and chemical properties of the polymeric materials. Attempt are also made to chemically attach the star-like polymers [16–25] and dendritic macromolecules [26–28] as the polymeric fragment due to their globular three-dimensional structure which may lead to greater encapsulation to conducting fullerene clustered by insulating polymer layers and also due to their ability to form monofunctional, monodisperse materials of known molecular mass within molecular dimension range. Utilization of functionalized fullerene to conduct such reactions is an interesting area of recent research. Functionalized fullerenes retain the main characteristics of pristine fullerene but are easier to dissolve in common solvents and more amenable to further studies [29–34]. Although large number of reactions were carried out with mono and bis-derivatives, very little progress on the, multifunctionalized derivatives [34] have been made. Formation of large number of isomers and the difficulty of characterization of multifunctional fullerene derivatives by conventional spectroscopic methods usually used in classical organic chemistry may be one of the possible reason for the slow progress in this area [35]. Many derivatives have a great propensity to eliminate and reform the parent fullerene making it difficult to determine by mass spectroscopy [36] and even high field two-dimensional ^{13}C NMR need acquition times of days to get the spectra [37]. In spite of this, the NMR technique has been used as an important and powerful tools not only to elucidate the structure of the fullerene derivatives but also peak area integration ratio give the number of groups attached per fullerene [27,38,39]. NMR coupled with IR and UV analysis has been used successfully in accessing fullerene core dendritic polymer molecules [26]. X-ray photoelectron spectroscopy (XPS) and thermogravimetric analysis (TGA)–mass spectroscopy measurements are other techniques used to estimate the number of hydroxyl groups in fullerenol [40]. In case of polydispersed molecules, the

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molecular mass of the dendritic polymer was determined by GPC and confirmed by light scattering measurements [41]. The conventional derivatization methods for hydroxyl groups are also being employed in couple of cases [42,43]. The weight gain in the products with respect to the substrates give the idea of number of groups attached (gravimetric method). Several other techniques are also used in tandem [43–45]. All the above methods, however, need extra precautions during sample preparation and the technical operation of these instruments is delicate. In comparison, the conventional thermal analysis techniques, like TGA and differential scanning calorimetry (DSC), are easier to operate and no extra precaution during sample preparation is required. Earlier we have exploited this technique (DTA and TGA) [46] for the characterization of trimethylol phenol not only with regards to its purity but also to corroborate existing theories regarding the mechanism of curing of PF resin and unambiguous and quantitative evaluation of the intermolecular condensation of methylols and intramolecular elimination of formaldehyde and the corresponding range of temperature for the onset and completion without resorting to any spectroscopic or chromatographic method.

This present article is mainly devoted to examine the capability of the simple thermal analyses techniques like TGA and DSC to calculate the number of addends on various fullerene derivatives. Applicability of these techniques were tested not only for simple fullerene derivatives like fullerenol but also with various fullerene core star-like macromolecules. A precise and concentrated effort has been made to show that only percentage weight loss calculated at particular temperature zone in TGA will be a critical parameter to estimate the number of addends with definite molecular mass like $-$OH and acrylate whereas the enthalpy changes in DSC associated with the dehydroxylation of unreacted $-$OH groups will be a useful parameter to calculate the number of addends having limited knowledge of molecular mass, like epoxy polymers. It has also been shown that these techniques are independent of the nature of the products formed. Whereas, the fullerenol and fullerenol-*n*-butyl acrylate condensates are highly soluble in water, the fullerenol-epoxy condensates are insoluble in water. It may be envisaged here that in the entire analysis no attempt has been made to study the thermal degradation mechanism of the products and the entire analysis was carried out without resorting to any spectroscopic or chromatographic methods.

2. Experimental

2.1. Instrumentation

Fullerene derivatives were characterized by spectroscopic and thermal methods. Infrared (IR) spectra were recorded on a Nicolet MAGNA IR-750 Spectrometer using solid solution in anhydrous potassium bromide as pallets. The UV-Vis spectra of the products were recorded on a Varian-CARY-500 UV-Vis–NIR spectrophotometer in dilute aqueous solution at equal concentration using redistilled water as the standard reference. The scanned wave length ranged from 200 to 800 nm. The enthalpy change associated with the dehydroxylation of fullerene derivatives was determined using differential scanning calorimetry at a heating rate of 10 °C/min upto 500 °C using a TA Instrument Inc. Thermal Analyst System model 2100 equipped with a model 2910 DSC Cell. The sample compartment was purged with dry nitrogen at 50 ml/min. The percentage weight loss and thermal degradation characteristics of samples were evaluated by thermogravimetry (TG) recorded on a TA instrument model Hi-Res-2950 TGA unit interfaced with the TA Instrument Inc. Thermal Analyst 2100 (Du Pont) control unit. The TGA cell was also purged with nitrogen at 50 ml/min during degradation runs. The amount of sample taken was approximately 5 mg in a platinum sample pan. The heating rate in each run was kept at 10 °C/min.

2.2. Estimation of number of substituents attached per fullerene

Assuming the percentage weight loss in temperature range of 150–570 °C corresponds to the removal of all the addends per fullerene $= x$ and, the percentage weight loss above 570 °C (correspond to the structural degradation of fullerene) plus the char yield is due to fullerene only $= y$. Then the number of groups attached per fullerence is given by

$$\frac{720}{y} \times \frac{x}{m} \tag{1}$$

where m is the weight of each group attached, e.g., $m = 17$ for $-$OH group. Calculating x and y from TGA thermogram, one can easily calculate the number of groups attached per fullerene from Eq. (1).

Now, if M is the molecular mass of the addend reacted with fullerenol, then $M/17$ is the hydroxy group equivalent per added group. For example, $M = 128$ for *n*-butyl acrylate, then $128/17 = 7.5$ hydroxy groups are equivalent to one *n*-butyl acrylate unit.

In case of polydispersed compound (e.g. polymers) with no definite molecular weight, the enthalpy change associated with dehydroxylation of products compared to fullerenol (in DSC) gives a clear idea about the number of groups attached (detail discussion in results and discussion section).

2.3. Synthesis of fullerene derivatives

2.3.1. Synthesis of fullerenol

The fullerenol used in these reactions was prepared by the reaction of fullerene in toluene and aqueous sodium hydroxide at ambient temperature using tetrabutylammonium

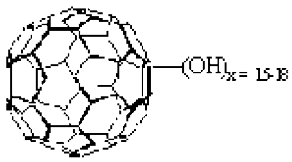

Fig. 1. Hydroxy fullerene.

hydroxide (TBAH) as phase transfer catalyst [43]. The structure (Fig. 1) of the resulting fullerenol was characterized by elemental analysis and various spectroscopic methods (IR and ^{13}C NMR).

2.3.2. Synthesis of fullerenol-epoxy star polymer

A novel ether connected epoxy star-like polymer (Fig. 2) was synthesized by selective reaction of fullerenol with a commercial grade cycloaliphatic epoxy resin (CY-230, Ciba Geigy) in heterogeneous medium at ambient alkaline condition using TBAH as phase transfer catalyst [47]. The progress of the reaction was monitored by FTIR analysis of the product formed.

2.3.3. Synthesis of acid and based catalyzed fullerenol-n butyl acrylate star polymer

A novel water soluble hydroxy-ether terminated heterocyclic star-like macromolecule (Fig. 3a) containing fullerene as a molecular core was synthesized via successive 1,2 Michael addition followed by nucleophilic addition reaction to carbonyl group of an α, β unsaturated ester (*n*-butyl acrylate) with fullerenol in aqueous solution in the presence of an acid [48]. The base catalyzed enol–ether terminated star-like macromolecule (Fig. 3b) was synthesized by the reaction of fullerenol with *n*-butyl acrylate in heterogeneous medium using TBAH as phase transfer catalyst via 1,4-Michael addition [48]. The progress of reactions was monitored by FT–IR and the nature of the products formed was analyzed by both FT–IR and UV-Vis spectroscopy.

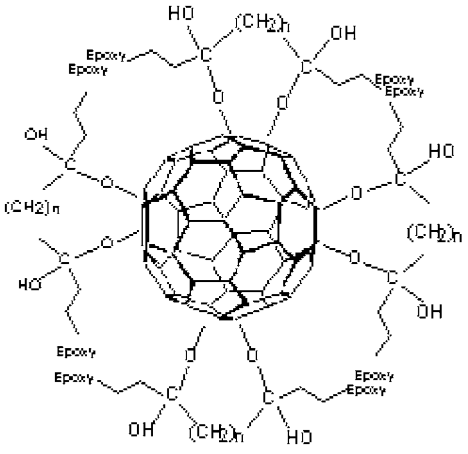

Fig. 2. Fullerene cored epoxy star polymer.

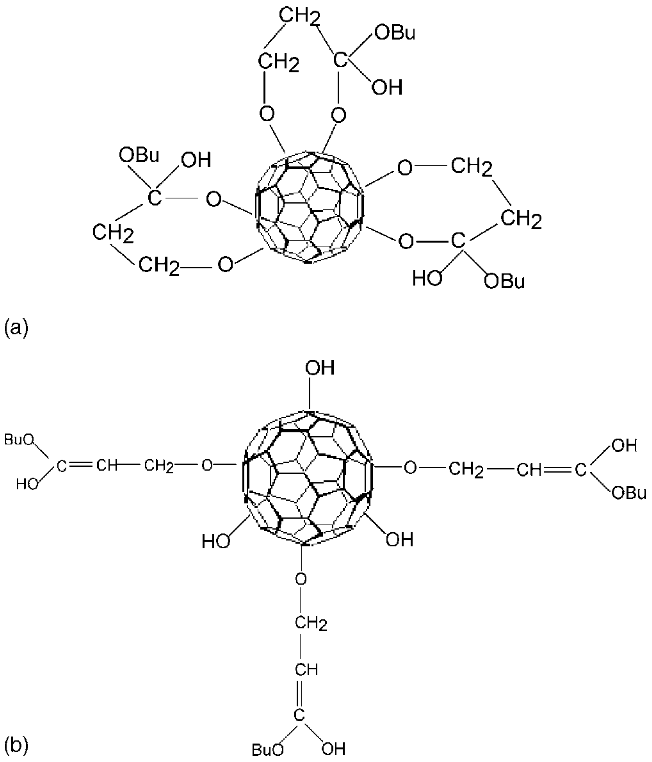

Fig. 3. (a) Acid catalyzed fullerene cored hydroxy-ether terminated star-like macromolecule. (b) Base catalyzed fullerene cored enol-ether terminated star-like macromolecule.

3. Results and discussion

3.1. Estimation of number of –OH groups per fullerene in fullerenol

Following TGA (Fig. 10a) and first derivative TGA trace of fullerenol [47,48], it can be easily argued that dehydroxylation of polyols have started at around 150–160 °C and all important and interesting chemical events which include dehydroxylation, hemiketal formation and pinacol type rearrangement of fullerenol and their degradation have taken place between temperature range of 150–570 °C before the structural degradation of actual fullerene. Detection of carbon dioxide due to thermal cleavage of dioxygenated carbon, such as hemiketal at low temperature (175 °C) and CO and CO_2 at the temperature up to 450 °C supports our argument [40,49]. Percentage weight loss between temperature range 150° and 570 °C was found to be 21% and the structural degradation of fullerene plus char yield contributes 57%. Then, the number of –OH groups attached per fullerene was calculated using Eq. (1) will be

$$\frac{720}{57}\times\frac{21}{17}=16$$

which nicely matches with the reported [47] value of 15–18. DSC trace (Fig. 4) of fullerenol shows an endothermic change in the temperature range of 125–275 °C with peak at ∼165 °C. The accompanied enthalpy change is 385 J/g.

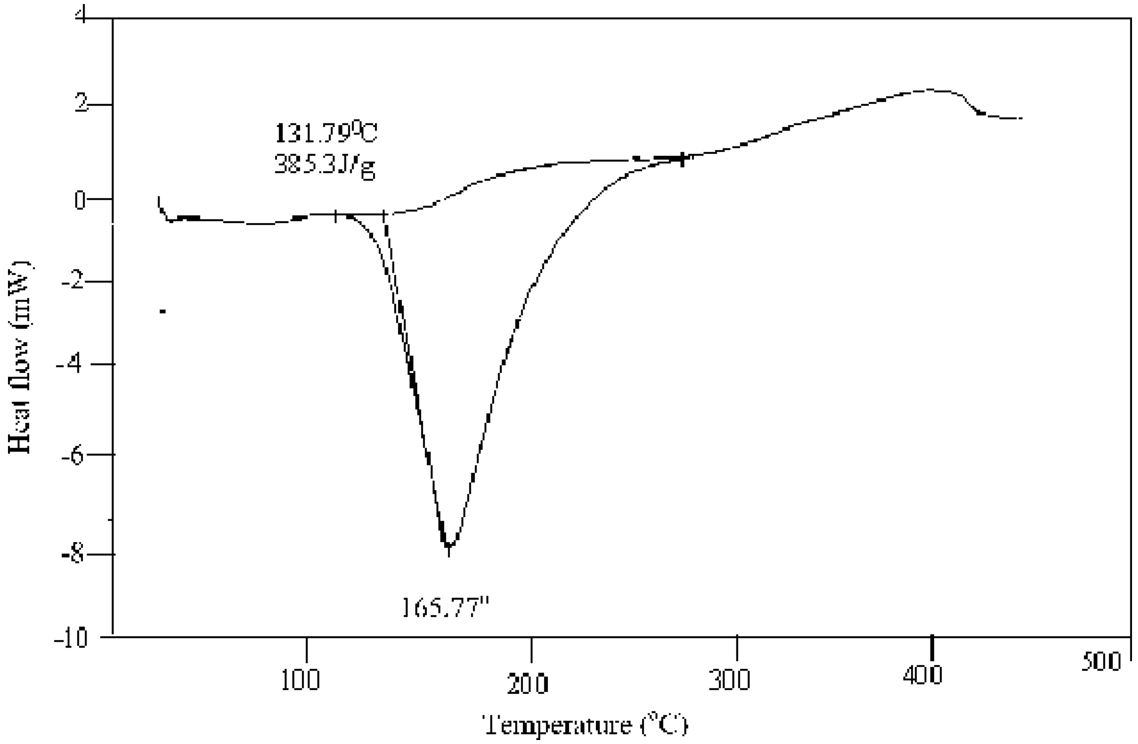

Fig. 4. DSC thermogram of fullerenol in N_2 atm.

Since all the 16 −OH groups are in free state in unreacted fullerenol, it is attributed that this enthalpy change (385 J/g) is definitely associated with the dehydroxylation of the 16 −OH groups.

3.2. Estimation of number of epoxy units attached per fullerene in epoxy star polymers

Credence to the above explanation is further provided by the thermograms of epoxy-fullerenol star-like macromolecules. In the DSC traces of the products at lower level of condensation, a distinct stepwise dehydroxylation can be observed. The level of the free hydroxyl groups in these products have been calculated from the enthalpy changes associated with the dehydroxylation of product collected in that particular zone. Thus, the DSC thermograms of epoxy-fullerenol condensates after 30 h (Fig. 5) and 50 h (Fig. 6) of reactions show enthalpy changes associated with dehydroxylation of free hydroxyl groups equal to 205 and 180 J/g, respectively. The level of the free hydroxyl groups

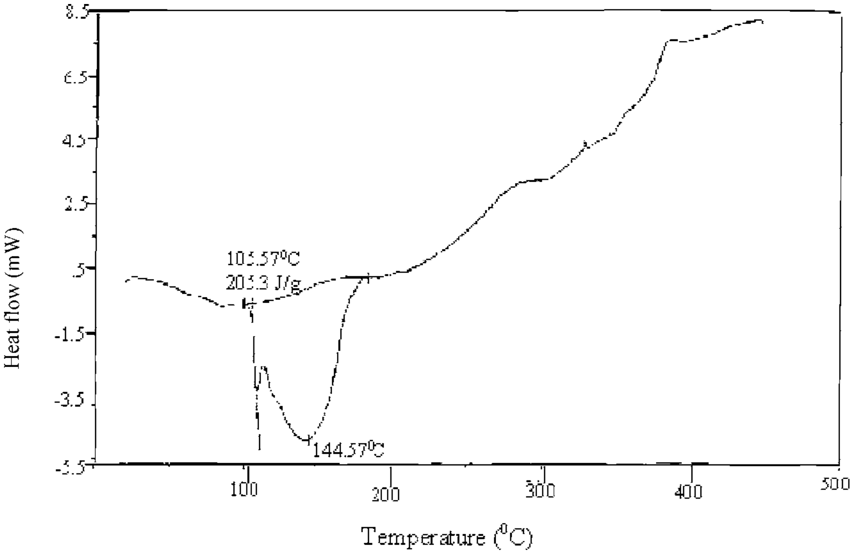

Fig. 5. DCS thermogram of epoxy-fullerenol condensate after 30 h of reaction in N_2 atm.

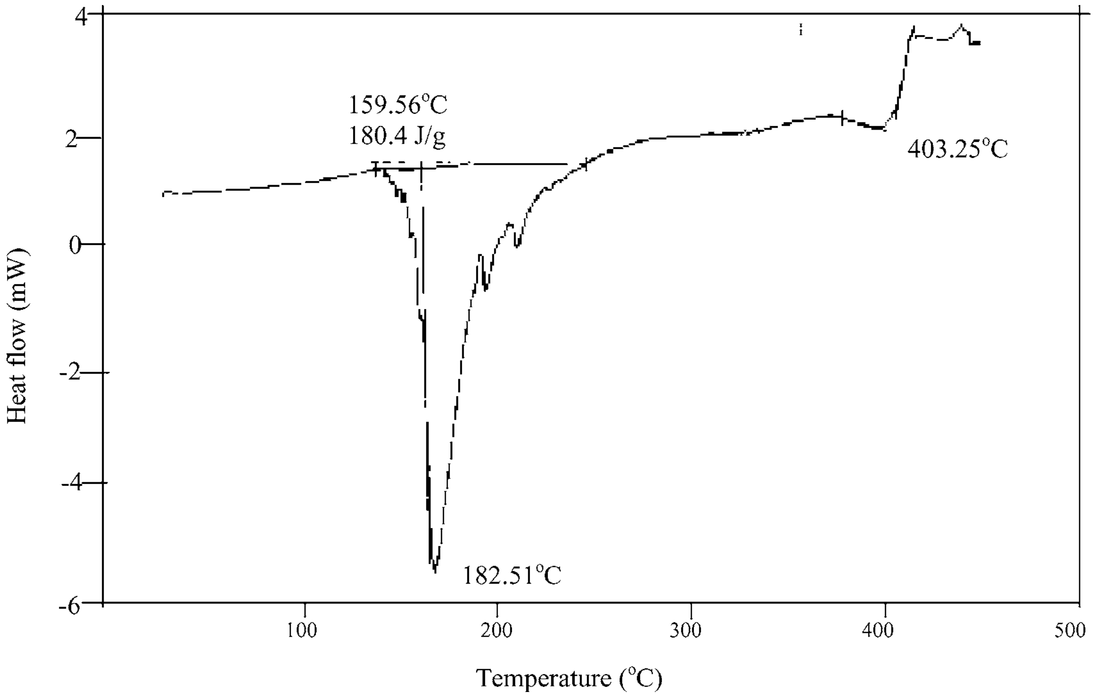

Fig. 6. DCS thermogram of epoxy-fullerenol condensate after 50 h of reaction in N_2 atm.

in these condensates has been calculated by comparing the enthalpy change associated with unreacted fullerenol to that of the products. They are about 9 and 7 free −OH groups per buckyball, respectively. Assuming 16 −OH free groups per buckyball in the unreacted fullerenol, the number of hydroxyl groups of fullerenol being consumed during that time intervals are about 7 and 9, respectively.

The cycloaliphatic epoxy resin (CY-230) employed in the present reaction contains two active carbonyl functional groups per molecule. This indicates 4 and 5 epoxy units are chemically attached per fullerene after 30 and 50 h of reactions. Also, the distinct step-wise dehydroxylation in the DSC traces of the products give a clear indication of neighboring group effect on the dehydroxylation steps and dehydroxylation steps occur at more specific temperature compared to unreacted fullerenol. The dehydroxylation is well separated from the endothermic degradation of the condensed hemiketal groups, which takes place in the temperature range of 360–400 °C (Fig. 7). The first derivative TGA trace of the condensate, however, did not show any impression of this stepwise degradation (Fig. 7).

At the highest achievable level of condensation, the product (after 80 h of reaction) in its DSC trace (Fig. 8) offered an enthalpy change of 57 J/g corresponding to about 2 free hydroxyl groups per C_{60} unit. This implies that 7 epoxy units are chemically attached per fullerene, consistent with our reported value of 6–8 [47]. The temperature range of dehydroxylation also came down to 120–200 °C, with a peak temperature of only 137 °C. The impression of stepwise dehydroxylation is also clearly visible. The first derivative TGA trace of the product (Fig. 9) is particularly unique in the sense that there is no impression of stepwise dehydroxylation in the lower temperature range (up to 170 °C). Instead, there is a monotonic weight loss up to 250 °C and then a sharp weight loss between the temperature 250° and 450 °C (crest temperature 355 °C) due to degradation of C_{60}-hemiketal groups in distinct steps, identifiable as short but sharp spikes superimposed over the Gaussian peak between 250 and 430 °C. Evidently, the C_{60}-hemiketal bond is much stronger than the C_{60}–OH bond, which is responsible for the observed greater thermal stability.

In the epoxy-fullerenol condensates, the percentage weight loss between temperature 150° and 570 °C in TGA have not been used to calculate the number of addends per fullerene because of the limited knowledge about the molecular weight of epoxy resin. Of course, the higher percentage weight loss of the product compared to unreacted fullerenol in the temperature range of 150–570 °C gave ample evidence of the degradation of high molecular material (epoxy units) chemically attached to fullerene.

3.3. *Estimation of number of n-butyl acrylate unit attached per fullerene*

The percentage weight loss obtained from the TGA trace of the product between the temperature range of 150–570 °C can, however, be uniquely employed to calculate the number of substituents attached per fullerene in case of an organic compound with known molecular weight. Calculating the total percentage weight loss of the products in terms of hydroxyl units between temperature range of 150–570 °C using

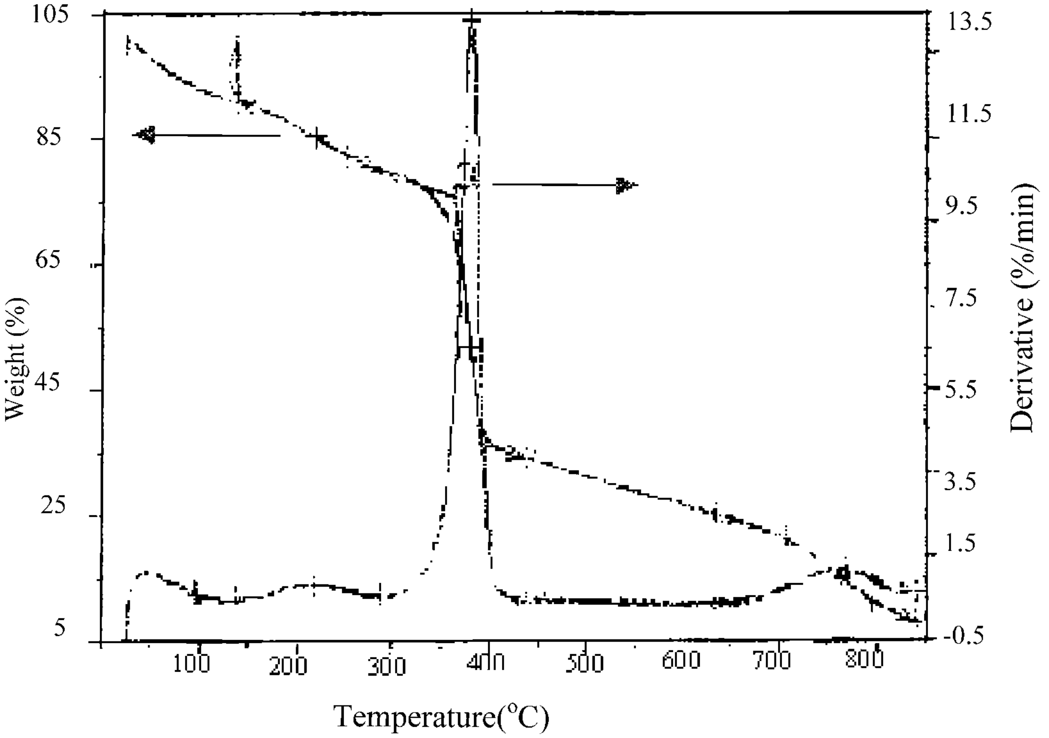

Fig. 7. First derivative TGA traces of epoxy-fullerenol condensate after 50 h of reaction in N_2 atm.

Eq. (1) and then subtracting the actual hydroxy units of unreacted fullerenol (i.e. 16 in the present case) gives the contribution due to organic units. Thus, about 40 and 36% weight loss between the range of 150–570 °C of acid and base catalyzed reaction products (Fig. 10b and c) of fullerenol and *n*-butyl acrylate corresponds to 4 and 3 acrylate units respectively which nicely matches with our reported value [48]. Each *n*-butyl acrylate (molecular weight = 128) unit can be considered as 7.5 hydroxy equivalent (128/17 = 7.50).

3.4. Estimation of acrylate units attached per fullerene in acid catalyzed reaction

Percent weight loss in the temperature range 150–570 °C = 40.5.

Percent weight loss in the temperature above 570 °C plus char residue = 41.3.

The total number of hydroxy groups equivalent per fullerene = $(720/41.3) \times (40.5/17) \approx 42$.

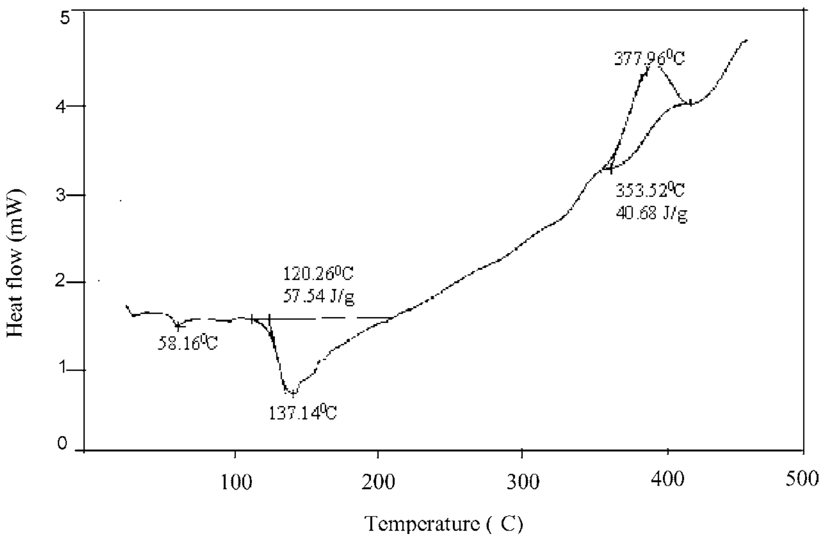

Fig. 8. DCS thermogram of epoxy-fullerenol condensate after 80 h of reaction in N_2 atm.

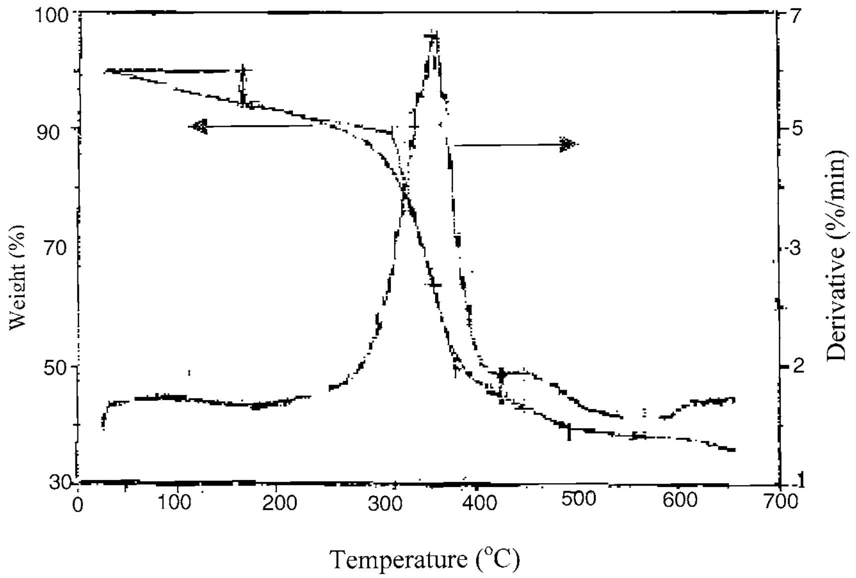

Fig. 9. First derivative TGA traces of epoxy-fullerenol condensate after 80 h of reaction in N_2 atm.

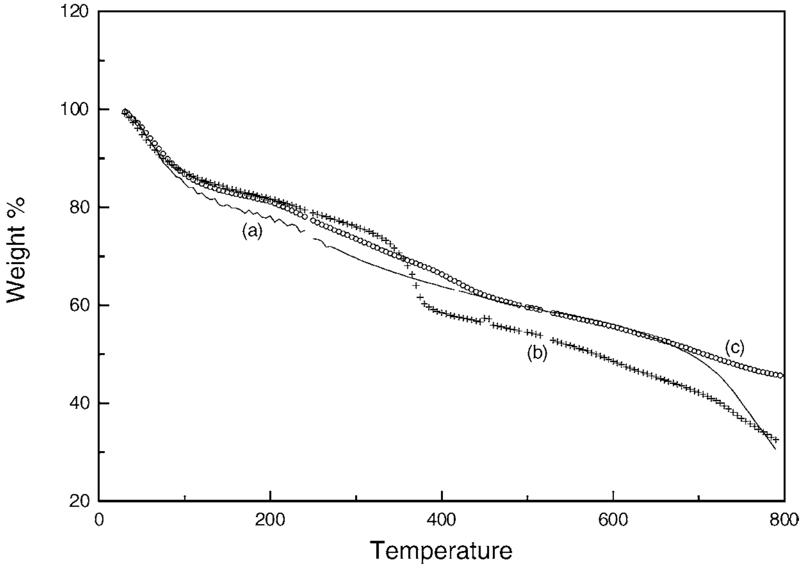

Fig. 10. TGA thermograms of (a) fullerenol; (b) acid catalyzed fullerene core hydroxy-ether terminated star macromolecule; (c) base catalyzed fullerene core enol terminated star macromolecule in N_2 atm.

Since there are about 16 –OH groups in unreacted fullerenol, then contribution of acrylate units $= 42 - 16 = 26$ hydroxy groups.

Since 7.5 hydroxy group is equivalent to one acrylate unit (molecular weight = 128).

Then number of acrylate units attached per fullerene $= 26/7.5 = 4$ (since molecule cannot be fractioned).

In a similar manner, the number of acrylate units attached per fullerene in base catalyzed reaction was calculated to be 3.

4. Summary and conclusions

Besides the usual application of DSC and TGA to study the stability and thermal behaviour, these techniques have been uniquely employed to evaluate the number of substituents attached per fullerene. The DSC thermograms of the epoxy-fullerenol condensates obtained at different time intervals (e.g. 30, 50 and 80 h) are helpful to evaluate the number of epoxy units attached in fullerene. On the other hand, TGA thermograms of acrylate-fullerenol condensates in both acid and alkali catalyst are sufficient enough to calculate the number of acrylate units attached in fullerene. Both soluble and insoluble fullerene derivatives have been easily evaluated by these techniques. The fullerenol-epoxy condensates are insoluble solid material whereas fullerenol-acrylate condensates are highly soluble in water. Also, this method is independent of the nature of the groups attached and equally applicable for both polydispersed materials as well as organic molecules having known molecular mass.

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