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Synthesis of dumbbell shape hyperbranched polymer: Based on diethylene triamine and acryloyl chloride used as rheology modifier for water based paints

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ABSTRACT

Hyper-branched polymer derived from ABx-type monomers have been generally recognized as the cheaper and economically more feasible counterparts of the well-known other members of the dendritic macromolecule family, the perfectly branched dendrimers. Since they can be manufactured more quickly and easily in a one-step polymerization procedure, their significantly lower cost price puts them in a much more favorable position to be industrially applied as coating resins. The conceptual design of a branched macromolecule is ideally outlined for film forming applications. The viscosity in relation to their molecular weight is kept low due to their compact morphology hampering chain entanglements, while on the other hand, the large number of functional end groups enable efficient cross-linking. In connection with studies of cyclic polymerisation the aliyl derivative of diethylenetriamine (DETA) has been prepared and hyper-branched polymer of Diethylene Tri amine (DETA) and Acryloyl Chloride (ACl) were successfully prepared by divergent approach. This hyper-branched polymer was comprehensively characterized by ^{1}*HNMR,* ^{13}*CNMR, mass spectroscopy, and FTIR*

Key Words: Hyperbranched Polymers, Convergent Approach, ^{1}HNMR, ^{13}CNMR , Water Based Paint, Rheology Modifier.

INTRODUCTION

The syntheses and the characteristics of novel polymeric architectures have become the subjects of increasing interest amongst polymer scientists over the last decades [1]. Properties of three-dimensional polymeric architectures do not only fascinate the academic research through their complexity and synthetic challenge [2], but they also get more and more attention in industrial research and application [3]. The class of dendritic polymers is divided into two different classes: the monodisperse dendrimers and the polydisperse hyper-branched polymers [4]. Dendritic polymers are especially attractive for industrial purposes, offering high functionality, broad variety of functional groups, high solubility and unique rheological behavior. These offerings make them ideally outlined for film forming applications. The viscosity in relation to their molecular weight is kept low due to their compact morphology hampering chain entanglements, while on the other hand, the large number of functional end groups enable efficient cross-linking. In terms of general coating practice, this means the combination of good flow and reduced solvent content with excellent chemical resistance, durability and good mechanical properties.

The maximum degree of branching, resulting from an exactly defined and perfect geometry, is found with the dendrimers, which are further characterized by a large number of reactive end groups, a spherical shape, and the possibility to take up guest molecules between the branches of the dendrimer host. Currently, two dendrimers, Starburst (polyamidoamine) and DSMs Astramol TM (polypropylene–imine) are commercially available. The synthesis of dendrimers is affected through a large number of subsequent steps, which necessarily lead to a relative high cost price, and limits their use in high added value applications.

Hyper-branched polymers have been generally recognized as their potentially cheaper and economically more feasible counterparts [4]. Since they can be manufactured more quickly and easily in a one-step polymerization procedure, their significantly lower manufacturing cost puts them in a much more favorable position to be industrially applied, especially as coating resins. A prerequisite for real commercial attractiveness is, of course, that these hyper-branched structures are built from commodity raw materials.

The principal concepts of the syntheses of hyper-branched polycondensates are already known for nearly 50 years, described by Flory [5]. The first report on the synthesis of hyper-branched structures from commodity chemicals, albeit “unintentional”, is even older, from 1929, when Kienle et al. [6] reacted glycerol with phthalic anhydride and realized only 10 years later that this synthesis afforded a resinous product with a “three-dimensional complexity”. Since then, a lot of hyper-branched structures have been described, however, from more elaborate building blocks. Most of the hyper-branched polymers reported are synthesized out of the so-called “AB_2” monomers, as described, for example by Fréchet and co-workers [7], who used 3,5-bis(trimethylsiloxy)-benzoyl chloride, Kim and Webster [8] (3,5-dibromophenyl)boronic acid (Suzuki conditions), Malmström and Hult [9] 2,2-bis(methylol)propionic acid, Kricheldorf and Stöber [10] silylated 5-acetoxyisophthalic acid and recently, trimethylsilyl-3,5-diacetoxybenzoate, Feast et al. [11] diethylhydroxyglutarate. In this “AB2” description A and B stand for independent functional groups which are preconditionally only reactive with one another and not amongst themselves, Fig. 1. Reaction of A-groups amongst each other would give rise to the formation of very low molecular weight structures instead of polymers; reaction of B-groups among each other, on the other hand, will cause gel (i.e. network) formation. Polycondensation of this monomer type will lead to highly branched tree-like structures with one A-group and .*n*C1/B-groups in each molecule (wherein *n* stands for the degree of polymerization), provided that a particular A-group would not accidentally react with a B-group within the same growing chain, in which case a cyclic structure would arise. In principle, the molecular weight would rise to infinity when the polycondensation degree of the AB2 monomer type would reach to unity. As a consequence, such a reaction is difficult to handle in industrial practice where large or variable molecular weights hamper the processability (Fig. 1, top diagram). Similarly, copolymerization of A2 and B3 or other monofunctional monomers also can give rise to hyper-branched structures, if the polymerization is kept below the gel point by either limiting the degree of polymerization or by changing the stoichiometry of these two reactants. Whereas an excess of the A2-units would inevitably lead to gel formation, a sufficient excess of the B3-unit could give rise to rather low molecular weight hyper-branched oligomers carrying B-end groups exclusively when the reaction degree reaches unity. In this approach, an industrial scale-up in a batch-wise production process would be feasible, since a predictable and stable molecular weight, and thus viscosity and processability, can be obtained without the risk of gelation. However, because of lack the of selectivity between the A- or B-groups within the same monomer unit, this method is limited to the oligomers and will fail to give higher molecular weight polymers without gel formation

Because of their good solubility and excellent processibility, three-dimensional hyper-branched conjugated polymers are attracting more and more attention as novel optical, electronic and magnetic materials. Hyper-branched polymers are receiving more attention as a biocarrires and biodegradable materials. Based on their unique properties, hyper-branched polymers can be applied as tougheners for thermosets curing, cross-linking or adhesive agents, dye-receptive additives for polyolefins, compatilizers, dispersers, processing aids, and rheology modifiers or blend components.

Now a days the hyper-branched polymeric dispersants are use to disperse pigment particles. The large number of the functional groups on the hyper-branched polymers has a significant influence on the final physical and chemical properties. This allows various possibilities to use these groups to obtain a certain desired property, such as reactivity, viscosity, compatibility or solubility and the use in different applications. The linear polymeric dispersants have pendent polar functional groups called as anchoring groups, which are designed to adsorb on to the pigment surface, therefore enveloping the pigment particles with the polymeric dispersant. Such polymers with pending polar group can interact inter and intramolecular or with functional group of binder molecules by polar forces i.e. chain entanglement, which increase the viscosity of the paint, whereas the hyper-branched polymeric dispersants have low viscosity at high molecular weight due to reduced chance of chain entanglement.

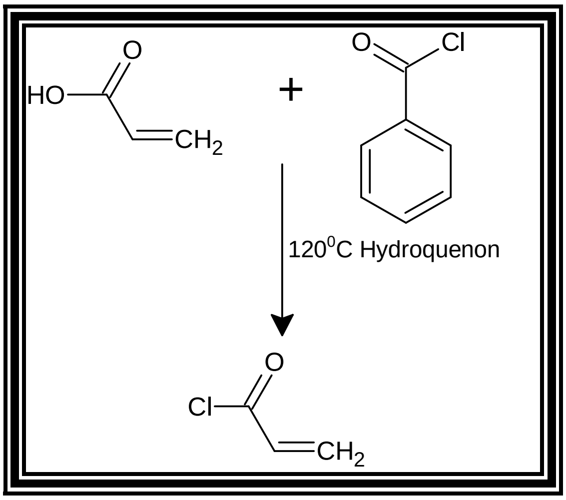
MATERIALS AND METHODS

Materials

Chemicals	Procured from	Purity %
Acryloyl Chloride	Synthesized in laboratory	95
DETA	s. d. fine chem. ltd	99
Benzoyl Chloride	s. d. fine chem. ltd	99
Acrylic acid	s. d. fine chem. ltd	99
Hydroquinone	s. d. fine chem. ltd	99
Xylene	s. d. fine chem. ltd	99
DMF	s. d. fine chem. ltd	99
Tio_2	West Coast Laboratories	-
Talc	DuPont India. Pvt. Ltd	-
$CaCO_3$	DuPont India. Pvt. Ltd	-
China clay	West Coast Laboratories	-

Synthesis of Acryloyl Chloride

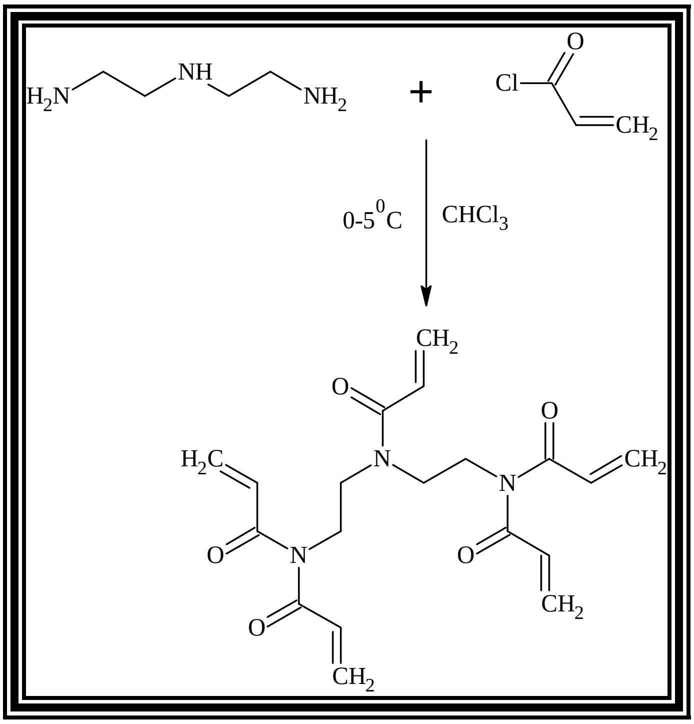
Acryloyl Chloride was prepared by reacting acrylic acid with benzoyl chloride following the procedure of Stempel et al. First, 3 mol of benzoyl chloride and 1mol of acrylic acid were mixed in a 250-mL, round bottom flask equipped with a condenser and thermometer, The mixture was heated to 120°C in an oil bath for 7Hrs, and the acryloyl chloride was distilled at 74^0-76°C and stored in amber colored bottle to prevent photo induced polymerization. The reaction yield was 85%. The reaction scheme is shown in Scheme No. 1



Scheme No. 3.1: Synthesis of Acryloyl Chloride

Synthesis of hyper branched polymer:

Hyper-branched polymer was synthesized by simple addition polymerization technique with the use of Diethylene Triamine (DETA) (0.5mol) and Acryloyl chloride (2.5mol). DETA is dissolved in Triethyl amine and chloroform cooled to 0-5 ^{0}C and under stared conditions freshly prepared acryloyl chloride was added drop wise over a period of 2 hrs. The progress of the reaction was monitored by FTIR to ensured maximum yield of the product. This solution was then treated with sodium bicarbonate to remove the unreacted acryloyl chloride, which helping in separating the desired end product from the unreacted compound. And finally the chloroform is evaporated on Rotavapor at a temperature of 45^0C to get final product. The reaction scheme is shown in Scheme No. 2



Scheme No. 3.2: Synthesis of Hyper-branched Polymer

Water based paint formulations

The water based paint was prepared having 45% PVC, 1.40 wt/l and the styrene acrylic emulsion having 50% NVM. The concentration of Hyper-branched polymer were varied from 0.5%, 1% and 2%, the paint was then applied on asbestos panels and tested for its mechanical properties, as well as the rheological properties of the paint. The **table No.3.1** shows the water based paint formulations.

Table No. 3.1 Water based paint formulations

INGREDIENTS	ROLE	STD Paint	0.5% HBP	1% HBP	2% HBP
TiO_2	True Pigment	10.0	10.0	10.0	10.0
Talc	Extender	16.0	16.0	16.0	16.0
$CaCO_3$	Extender	20.0	20.0	20.0	20.0
Emulsion	Binder	25.0	25.0	25.0	25.0
Water	Solvent	24.0	24.0	24.0	24.0
Ethylene Glycol	Coalsing solvent	4.0	4.0	4.0	4.0
Hyper-branched Polymer (HBP)	W&D, Rheology Modifier, Flow & Leveling agent	0.0	0.5	1	2
Micronil	Biocide	0.5	0.5	0.5	0.5
Antifoam K-31	Deafomer	0.2	0.2	0.2	0.2
Buffer	Neutralization	0.1	0.1	0.1	0.1
Total		100	100	100	100

Characterization

Spectroscopic Analysis:

a) FTIR Spectroscopy

The FTIR spectra were recorded with a FTIR-8400S SHIMADZO Japan (Diamond ATR) infrared spectrophotometer. FTIR spectrum for HBP was evaluated using 0.5% KBr pallets.

b) NMR Spectroscopy

The ^{1}HNMR spectra were obtain with a VARIAN, USA mercury plus spectrometer operated at 300 MHz with chloroform as a solvent and the ^{13}CNMR spectra were obtain with a Bruker Avance 550 NMR spectrometer, USA. with Chloroform as solvent.

C) Mass Spectroscopy

The mass spectra were recorded on HPLC (Jasco 1090 series) equipped with a hypersil C-18 column (l=250 mm, d= 5mm) and the unsaturation/conjugation was determined by UV-spectroscopy.

d) Viscosity measurement

Viscosity of emulsion was measured using Brook Field viscometer (GMBH, Austria)

Mechanical Testing of Coatings

a) Scrub resistance test

It was performed according to ASTM 2486 – 79, the film results were given in cycles.

b) Pencil hardness test

It was used to observe the hardness values of the films according to ASTM D 3363.

c) Water Resistance

The coated panels were immersed in water, the panels were evaluated for color change of coating, blistering, skinning according to ASTM D 870-02.

d) Gloss @ 60^0

A Rhopoint-Novoglass glossmeter (Serial No 26135) was used to test the light reflection properties of the specimens according to ASTM D 523. The instrument was first calibrated for zero and then for the two standards supplied by the manufacturers. The coated asbestos panel was then placed with the coated surface facing upwards and the gloss measurements were determined. The average of the gloss measurements was taken as the specular gloss of the film.

RESULTS AND DISCUSSION

FTIR:

The synthesis rout of hyper-branched polymer is briefly shown in Scheme No. 2. FTIR is a graph between % Transmittance on Y axis and Frequency on X axis. Functional groups are characterized by its corresponding frequency. Figure No. 1 shows the FTIR spectra of Hyper-branched Polymer. There is no peak at 3345 Cm^{-1} which indicates the absence of primary amine (--NH). The ester group in FTIR shows a typical stretching absorption at 1745 cm^{-1}. The aliphatic C-H bond shows stretching absorption at 2979 cm^{-1}.

Mass Spectroscopy: Figure No. 2 shows the mass spectra of HBP. The synthesized hyperbranched polymer was analyzed using a high performance liquid chromatography (HPLC) (Jasco 1090 series), equipped with a Hypersil C-18 column (l: 250 mm, d: 5 mm). A mixture of acetonitrile – water in 55:45 ratio was used as the mobile phase with the flow rate of 1.0 cm^3/min. A PDA detector (JASCO MD 2010 series) was attached to the HPLC unit for detection. The product mixture was also subjected to the LC-MS analysis to characterize hyperbranched polymer, on a Finnigan LCQ Advantage Max mass spectrometer (LCQAD 30000, Thermo Electron Corporation), using the same column and mobile phase as the HPLC analysis. Pure and dry nitrogen was used as a sheath gas or nebulizer gas with a flow rate of 40 cm^3/ min and an auxiliary nitrogen gas flow rate was maintained at 18 cm^3/ min. The capillary temperature was maintained at 548K with the voltage at 420 V and the ion spray voltage at 5 KV. The spectra shows the exact molecular mass of hyperbranched polymer (found= 372, cal.= 373)

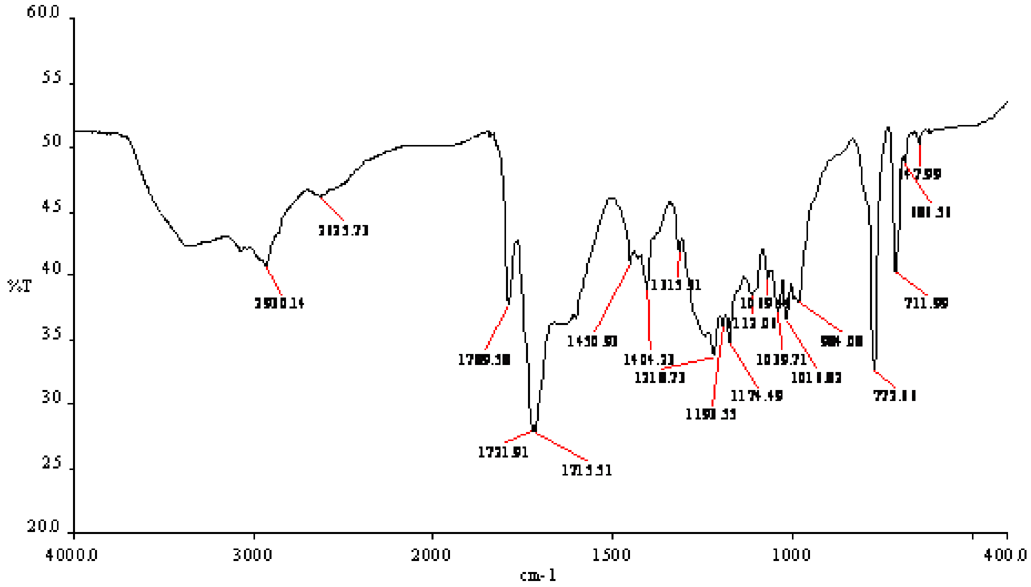


Figure No. 3.1: FTIR spectra of Hyper-branched Polymer

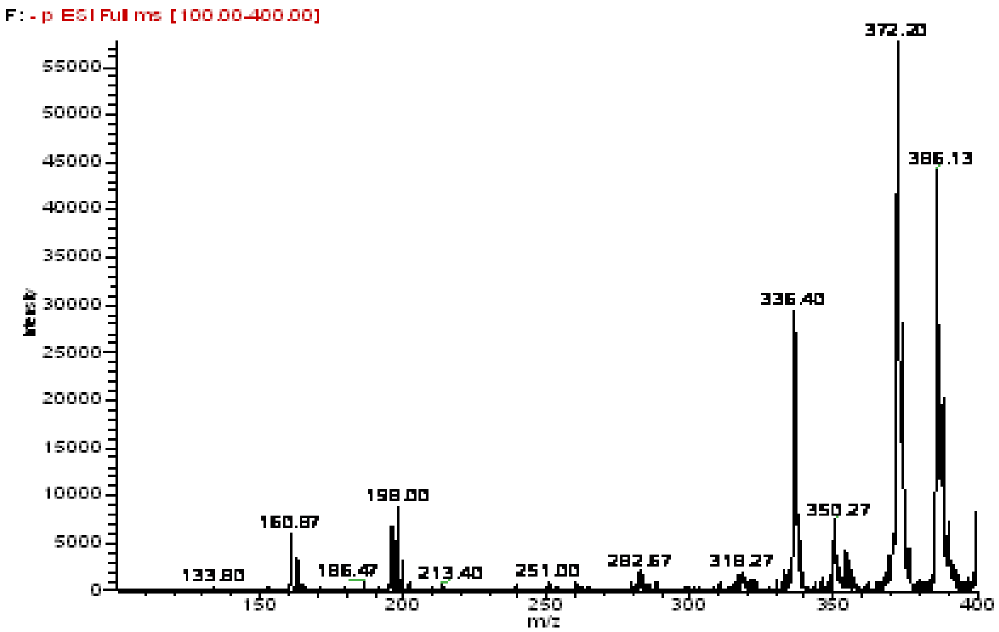


Figure No. 3.2: Mass spectra of Hyper-branched Polymer

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^{1}HNMR Spectroscopy

Figure No. 3shows the ^{1}HNMR spectra of Hyper-branched Polymer CH2 8.1 d, J=7.7, CH 7.47 t, J = 7.7, N-CH2-CH2 3.77, t, J= 6.6, N-CH2-CH2 2.86 t, J= 6.6, CH2-N=C=O 7.61 t, J= 7.3, CH2 7.8, t, J = 7.3

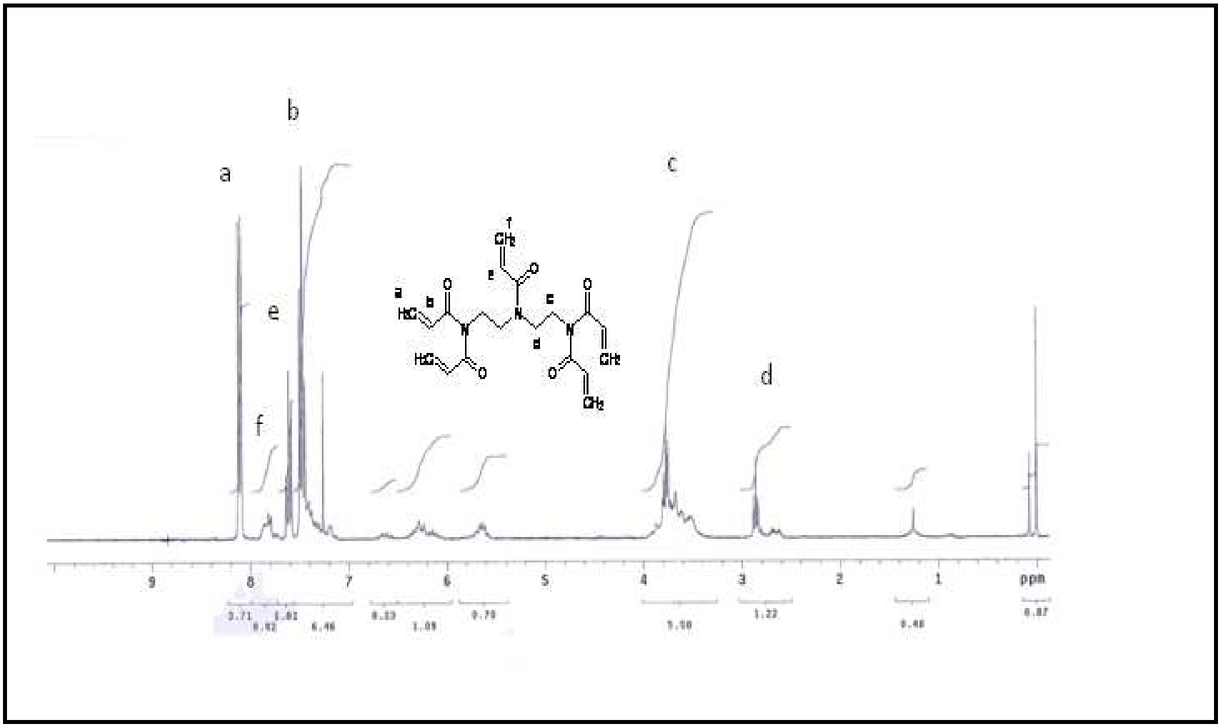

Figure No. 3.3: ^{1}HNMR spectra of Hyper-branched Polymer

Degree of branching

The degree of branching is commonly calculated according to the following equation:

$$DB = \frac{D+T}{D+L+T}$$

Where D, T and L are the fractions of dendritic, terminal and linear incorporated monomers in the resulting hyperbranched polymer. Thus using above equation the degree of branching of (HBP) hyper-branched polymer was found to be 0.78 which confirms the hyper-branched structure

^{13}CNMR Spectroscopy

Figure No. 4 shows the ^{13}CNMR spectra of Hyper-branched Polymer The spectra shows the positioning of the Carbon atom in the structure of hyper-branched polymers 174.5, 170.2, 132.5, 130.4, 129.56, 128.5, 38.9, 37.3 ppm

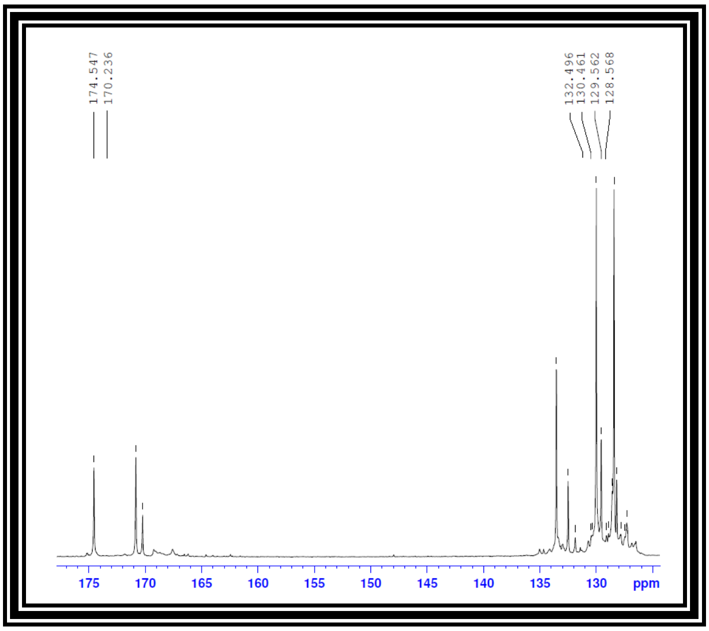

Figure No. 3.4: ^{13}CNMR spectra of Hyper-branched Polymer

UV Spectroscopy

Figure No. 3.5 shows the graph of UV- Spectra it shows the absorption value of 2.40 and the wave length 240, which indicates the presence of double bond i.e. conjugation, is intact in hyper-branched polymer.

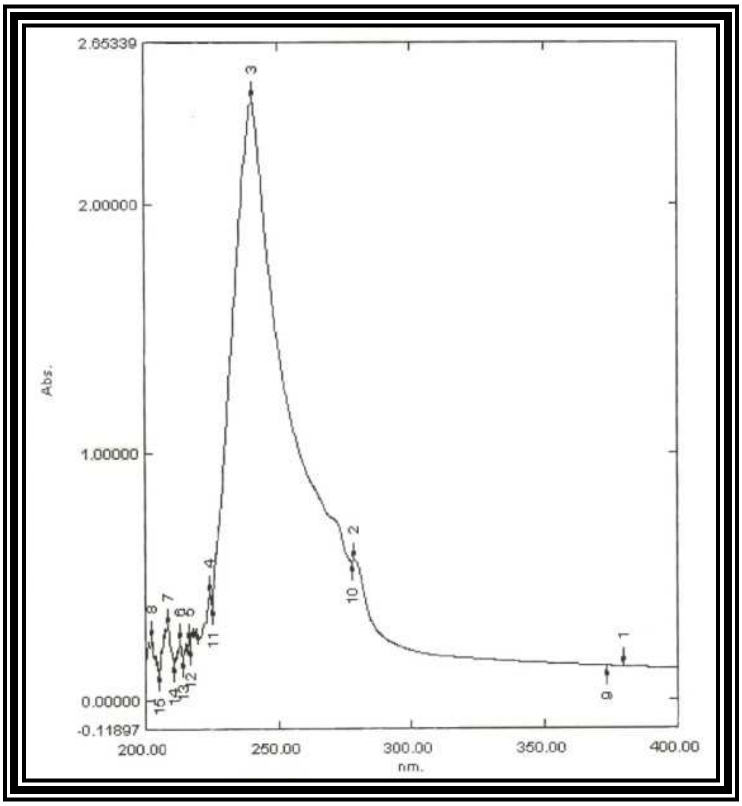

Figure No. 3.5: UV- Spectra of Hyper-branched Polymer

Viscosity measurements

The viscosity of water based paint was measured on Brookfield viscometer. By addition of Hyper-branched (HBP) additives there is a drastic change in viscosity was observed, without altering the physical, optical and mechanical properties of the final paint.

Table No. 3.2 Water based paint formulations

Samples	Viscosity Mpa	RPM	Efficiency
W/O Additives	1460	100	96 %
0.25%	1000	100	93 %
0.50%	670	100	93%
0.75%	670	100	90%
1%	660	100	91%

Coating Properties:

It was noticed that the coatings were uniformly colored and without any visible defects like pinholes, pitting, wrinkling, blistering etc regardless of the composition used. Dry film thickness (DFT) of the coating applied on asbestos panel was found to be 60-85 microns.

Table No.2.3 water based paint test results

Test Conducted	W/O HBP	0.5%	1%	2%
Brookfield Viscosity Cp	530	460	440	410
Stain Resistance	4	4	4	4
Weight per Liter	1.40	1.40	1.39	1.39
Covering Capacity Kg/M^2	12.0	12.6	13.2	13.5
Pendulum Hardness in counts	26	26	26	28
Dry Scrub	0.1	0.04	0.03	0.03
DFT Microns	60	55	50	50
Gloss @ 45^0	2.60	2.60	2.58	2.51

Scale for stain resistance: Excellent =5, Good =4, Poor = 0

Optical Properties:

The gloss of coated panels was measured using digital glossometer at 60^0. The gloss of HBP coating was observed to be slightly higher than that of the without HBP coatings which is a characteristic property of HBP network. The slightly lower in gloss was observed at higher loading of HBP that could be due to the presence of amine.

3.7.2 Mechanical Properties

a) Adhesion

The adhesion of the coatings to the asbestos substrate was investigated by cross-hatch method. It was observed that all the coatings showed excellent adhesion, to the substrate irrespective of curing chemistries. The polar nature of the hyper-branched polymer backbone containing diethylene triamine.

b)Pencil Hardness

The coating hardness was measured by scratch hardness and pencil hardness method. There was no significant difference observed in pencil hardness of HBP and without HBP coatings.

CONCLUSION

Cyclic polymerisation the aliyl derivative of diethylenetriamine (DETA) has been prepared and hyper-branched polymer of Diethylene Tri amine (DETA) and Acryloyl Chloride (ACl) were successfully prepared by divergent approach.

The mechanical performance of the HBP coatings was observed better as compare to without HBP coatings. Regardless of the excellent performance of HBP coatings, the system holds a major impact on reduced in viscosity of the final paint without altering mechanical as well as other properties of cured film.

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