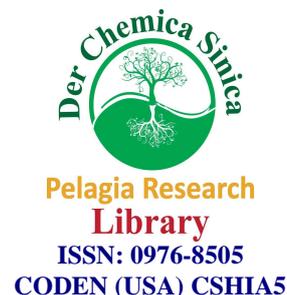




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### Hyperbranched polymers a rheology modifier for water based paints

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#### ABSTRACT

Hyperbranched copolymers of ethyl acrylate (EA) and tri methylol propane triacrylate (TMPTA) with different degree of polymerizations (DP-5, 8, 10, and 50) were prepared by convergent approach. Initially EA macroinitiator was prepared by Atom Transfer Radical Polymerization (ATRP) using N, N, N', N'', N''' pentamethyldiethylenetriamine (PMDETA) as a ligand, ethyl 2-bromoisobutyrate as an initiator and cuprous bromide (CuBr) as a catalyst, followed by subsequent copolymerization with trimethylol propane triacrylate (TMPTA). These hyperbranched copolymers were comprehensively characterized by Nuclear Magnetic Resonance Spectroscopy (<sup>1</sup>HNMR), Fourier Transfer Infra Red Spectroscopy (FTIR), Differential scanning calorimeter spectroscopy (DSC), RT- 10 Rheometer and Size Exclusion chromatography. These hyperbranched polymers were successfully used as rheological modifier in water based paints. The concentration of hyperbranched polymers used was 1 wt % in paint formulation and dramatic decrease in viscosity of paint were observed.

**Keywords:** Hyperbranched polymer, Degree of polymerization, Rheology, ATRP, NMR,

#### INTRODUCTION

'Hyperbranched polymer' was first coined by Kim *et. al.* in 1988 when they synthesized hyperbranched polyphenylene [1]. Hyperbranched polymers are by now an established class of polymeric materials and can be considered as highly functional specialty products. Since then hyperbranched polymers have attracted increasing attention owing to their unique properties and greater availability as compared with dendrimers [2]. They offer the chance for the development of new products but at the same time they present a challenge due to their complex branched structure [3]

The fundamental approach for synthesis of monodisperse hyperbranched polymer (dendrimers) requires absolute control of all synthesis steps, whereas polydisperse hyperbranched polymers are accomplished by a simplified approach similar to conventional resin technology. Atom Transfer Radical Polymerization (ATRP) is one of the most appropriate controlled radical polymerization technique which allows to tailor the different copolymers, star polymers and hyperbranched polymers of desired molecular weight, molecular weight distribution at atmospheric pressure and temperature slightly above the ambient temperature [4]

Hyperbranched copolymer of EA and TMPTA has been synthesized by ATRP via convergent approach. A tree structure begins to form when chain extenders react, either with a core or with other chain extenders. These may or

may not have the same type of reactive groups. Dendritic and hyperbranched structures can be produced in three different ways as published in the literature.

In the published literature hyperbranched polyphenylene, [5] polyesters, [6-7] polyethylene oxide [8] are well reported. There are also reviews on the synthesis properties and applications [9-13]

## MATERIALS AND METHODS

### 2.1. Raw materials

Ethyl Acrylate (EA) (Ranbaxy Fine Chemical Limited, India), Trimethylol Propane Triacrylate (TMPTA) (99%, Ranbaxy Fine Chemical Limited, India), Cuprous bromide (CuBr) (99%, Aldrich, India) was purified with glacial acetic acid, followed by ethanol and dried under vacuum. N, N, N', N'', N''' pentamethyldiethylenetriamine, PMDETA (99.9%, Merck, India), Tetrahydrofuran (99.5%, Merck, India), 1, 4-Dioxane (Ranbaxy Fine Chemical Limited, India) were used without purification. Styrene acrylic emulsion having Tg of 23°C was utilized for paint preparation.

### 2.2. Synthesis of macroinitiator of ethyl acrylate (EA) by using ATRP

The reactions were carried out in a flask fitted with pulley, inlet thermometer pocket, water condenser and nitrogen purger. The entire assembly was placed in a water bath connected to a temperature controller. The flask was completely blanketed with nitrogen throughout the reaction. EA was charged first, followed by CuBr under stirred condition to prepare homogenous solution. PMDETA was introduced in the reaction mixture to form a complex; and it was evident by color change from light green to dark green. Subsequently ethyl-2-bromoisobutyrate was added in the reaction mixture and temperature was maintained at 60°C. During the progress of reaction, the samples were drawn at regular intervals to check the conversion. The reaction mechanism was shown in scheme No. 2.

### 2.3. Synthesis of hyperbranched copolymer (EA-b-TMPTA) by convergent approach

Hyperbranched copolymers were synthesized by adding TMPTA in EA macroinitiator as prepared above. The mechanism of hyperbranched copolymer of EA-b-TMPTA is shown in Scheme No. 3. The simple addition reaction takes place and the unreacted monomer of EA work in controlling the viscosity and exotherm therefore there was no prerequisite of solvent for copolymerization. After the maximum conversion, the copolymerization reaction was stopped. The samples were heated to remove unreacted monomers. Purification of copolymers was done by dissolving them in 1, 4-Dioxane solvent and then passing through an aluminium column to remove metal complex.

### 2.4. Hyperbranched polymer as rheological modifier in water based paint.

Four different types of hyperbranched polymer were employed as rheology modifier in water based paint. The concentration of hyperbranched copolymers were 1 wt% in standard water based paint formulation. The recipe for water based paints is shown in Table No.1

## 3. CHARACTERIZATION

### 3.1. Fourier Transform Infrared Spectroscopy (FTIR)

FTIR measurements of the hyperbranched polymers were performed using a FTIR-8400S SHIMADZO Japan (Diamond ATR) infrared spectrophotometer.

### 3.2. Nuclear Magnetic Resonance (NMR)

The hyperbranched polymer was evaluated by NMR spectroscopy using a Bruker Avance 550 NMR spectrometer, USA.

### 3.3. Differential Scanning Calorimeter (DSC)

Thermal behaviors of hyperbranched polymers were studied by DCS 7, Perkin Elmer, USA to evaluate the glass transition temperature. The scanning rate was 10°C/min.

### 3.4. RT 10- Rheometer

The rheological properties of water based paints were measured by Haake Rheometer RT-10 Germany.

### 3.5. Size Exclusion Chromatography (SEC)

The structure of hyperbranched polymer was confirmed by the SEC (Viscotek Malven, UK) using ViscoGEL GMHxl 2x column and TDA302 detector.

### 3.6. Brookfield Viscometer (ASTM-D 2196)

The internal resistance or viscosity is typically measured using a rotating spindle instrument such as a Brookfield viscometer.

## RESULTS AND DISCUSSION

### 4.1. Hyperbranched Polymer

#### 4.1.1. Fourier Transform Infrared Spectroscopy (FTIR)

The Hyperbranched polymers were characterized by FTIR. The FTIR spectrum of the hyperbranched polymers of DP 8 and 10 are depicted in Figure No, 1 (A) and (B).

The absorption peak at  $1745\text{ cm}^{-1}$  indicates the presence of ester group. Absorption at  $2979\text{ cm}^{-1}$  shows the aliphatic C-H bond stretching and the absorptions at  $1446$  and  $1379\text{ cm}^{-1}$  shows C-O and C-Br stretching respectively.

#### 4.1.2. Nuclear Magnetic Resonance (NMR)

Figure No.2 shows the  $^1\text{H-NMR}$  Spectra of hyperbranched copolymer of EA and TMPTA. It is well known that EA shows double doublet at  $\delta=6.6$ , but the  $^1\text{H-NMR}$  analysis of final product shows there is no such double doublet at  $\delta=6.6$ , which confirms that there is a formation of hyperbranched polymer.

$^1\text{H-NMR}$  Spectra of hyperbranched copolymers of EA and TMPTA shows triplet of primary  $-\text{CH}_3$  group at  $\delta=1.1$ , singlet of secondary  $-\text{CH}_2$  group at  $\delta=1.2$ , singlet of  $\text{CH}_2-\text{COO}$  group at  $\delta=2.2$ , triplet of  $-\text{CH}-\text{CH}_2$  group at  $\delta=1.5$ , quartet of tert  $-\text{CH}$  group at  $\delta=1.9$ , singlet of primary  $-\text{CH}_3$  at  $\delta=1.6$ , quartet of  $-\text{COO}-\text{CH}_2-\text{CH}_3$  at  $\delta=3.7$  and doublet of  $\text{CH-Br}$  at  $\delta=4.1$ . All these  $\delta$  values for their particular groups confirm the formation of hyperbranched polymer.

#### 4.1.3. Differential Scanning Calorimeter (DSC)

Figure No.3 and 4 shows DSC thermograms of hyperbranched polymers with degree of polymerization 5 and 10 respectively. Theoretical Tg of EA and TMPTA is  $-24^\circ\text{C}$  and  $60^\circ\text{C}$  respectively. Theoretical Tg of polymer is  $-38^\circ\text{C}$ , and by DSC estimation shows it was  $-39.83^\circ\text{C}$  for DP-5 and  $-40.73^\circ\text{C}$  for DP-10 which is more closer to their theoretical values.

#### 4.1.4. RT 10- Rheometer

Figure No. 5 and Figure No. 6 shows graph of viscosity Vs shear rate of hyperbranched polymer for degree of polymerizations 5 and 10 respectively plotted with the help of RT 10 rheometer. The viscosity at very low shear rate shows some humps because the chains of neighboring molecules may entangle with one another. However as the shear rate raises the entanglements gets reduce because of the molecular orientation, which on further raise in shear rate don't alter the Newtonian flow behavior.

Both the graphs show unaltered viscosity with shear rate change in. which is an authentication of Newtonian fluids that are hyperbranched polymer.

#### 4.1.5. Size Exclusion Chromatography (SEC)

Figure No.7 depicts the molecular characterization of hyperbranched polymer with the help of triple detection by SEC, consisting of refractive index, light scattering and viscometer providing the requisite information about molecular weight, hydrodynamic radius and intrinsic viscosity respectively whereas the corresponding peak information is provided in Table No.2. The relative molecular weights of the polymeric sample determined through refractive index detector which is at 5448 Dalton. Light scattering detector provides information about viscosity measurements representing the solution properties of the species. Relationships between solution viscosity and molecular weight have been determined, Mark-Houwink constant ( $\alpha$ ) typically varies between 0.6 and 0.2, depending on the nature of the species present in the sample. The exponent is typically in the region of 0.6-0.8 for linear homopolymers in a good solvent with a random coil conformation however the values lie between 0.2 to 0.5 for branched polymers depending on the degree of branching. In this study, Mark-Houwink constant ( $\alpha$ ) values less

than 0.5 indicating very compact and branched structures. It is obvious that the viscosities of branched species are significantly lower than those of the linear ones based on the Mark-Houwink equation. Additionally, the radius of gyration ( $R_g$ ) values obtained via light scattering method also indicate a higher  $R_g$  due to its random coil like structure which have much more compact structure and constitute majority by mass of the sample. Whereas lower intrinsic viscosity detected also indicates that hyperbranched structure is present.

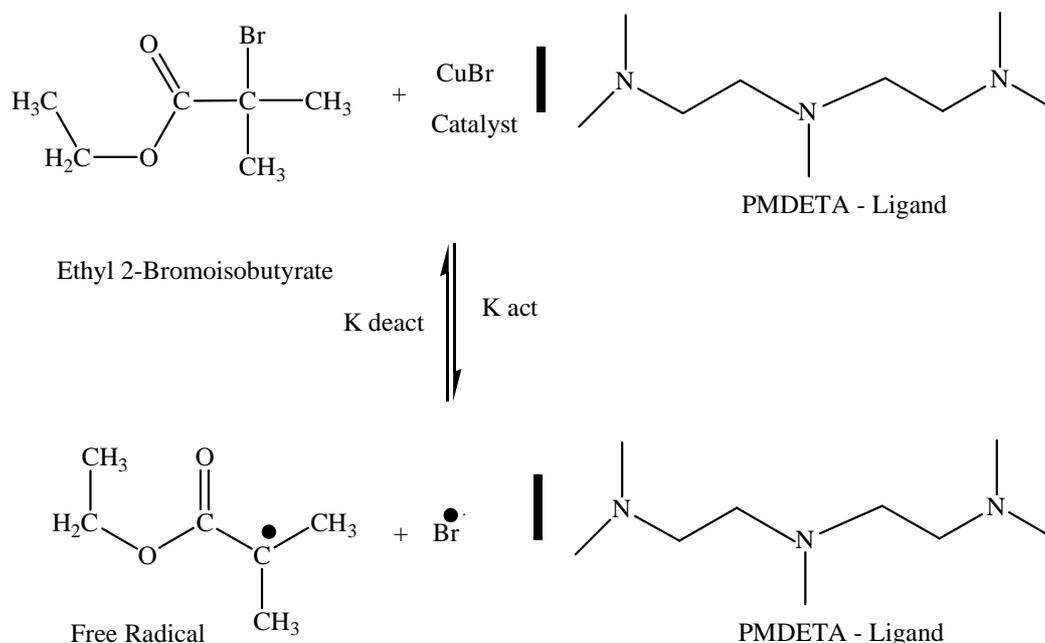
#### 4.2. Application of Hyperbranched Polymers As Rheology Modifier in Water Based Paints.

Polymers rheology by virtue of their high molecular weights, chain entanglements and polymer solvent interactions. In water borne acrylic dispersions the binder aggregates are dispersed and stabilized. This aggregates results in frozen stage of the binder resulting in poor flow and leveling. Hyperbranched copolymer of EA and TMPTA is used as rheological modifier in water based paint.

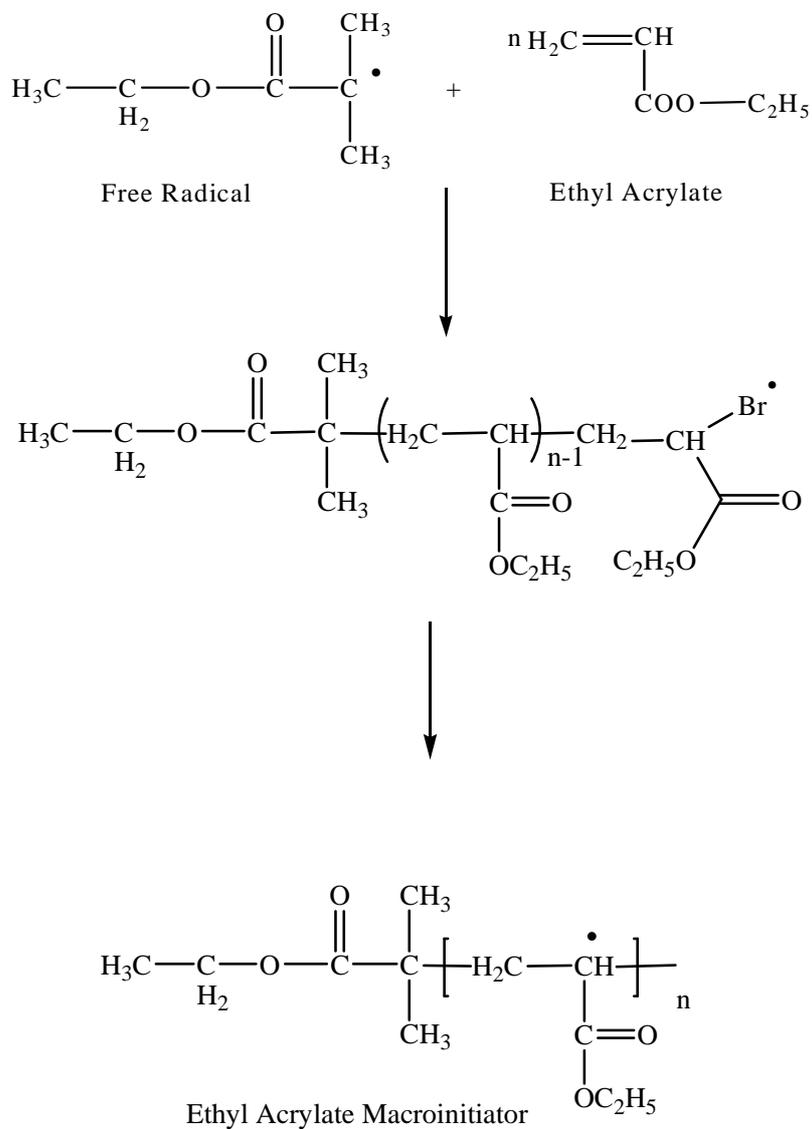
The graph of viscosity Vs rpm for emulsion paints with and without additives at 1 wt % is given in figure No-8 having Dp- 5, 8, 10 and 50. The viscosity of paint without additive is higher as compare to paint with additives at all rpm. There is sharp decrease in viscosity with increase in rpm for the additives with Dp-10. Whereas at higher molecular weight hyperbranched polymer i.e. Dp-50 the intermingling of the chains doesn't reduce the viscosity but rather shows hump at 30 rpm. However the viscosities of additives with Dp-10 is having the lowest viscosity, the ratio of the viscosity difference for Dp-50 and Dp-10 is 1.41 which shows the viscosity reduction is more at high rpm. Next step is to check whether decreased in viscosity due to rheological additive affect other properties of water based paint or not. For that purpose all types of water based paints were applied on asbestos sheet (7 cm \* 15 cm), their color values were checked by reflectance spectrophotometer color eye 7000 A, (Gretab-Macbeth, USA) and compared with that of without additive water based paint formulation.

Figure No.9 to Figure No.11 shows graph of % Reflectance Vs Wave Length for all DP's in comparison with and without additive. DP-50 also shows same behavior for graph of % Reflectance Vs Wave Length, since it is not giving good performance in rheology modification as compared to DP-5, 8, 10, it is not considered. From Figure No.11 to Figure No.13 it is conclude that reflectance values for all DP's and that of without additive formulation are almost same, so we can say that there is no change in optical properties of paint with addition of additive. Figure No. 11 confirms that addition of additives with different DP's doesn't affect whiteness index of water based paint. Whiteness index for water based paint without additive is 73.85.

Scheme No.1: The reaction scheme for hemolytic cleavage of initiator in presence of catalyst and ligand



Scheme No. 2: Formation of Macroinitiator of Ethyl Acrylate.



Scheme No. 3: Synthesis of Hyperbranched copolymer of EA and TMPTA

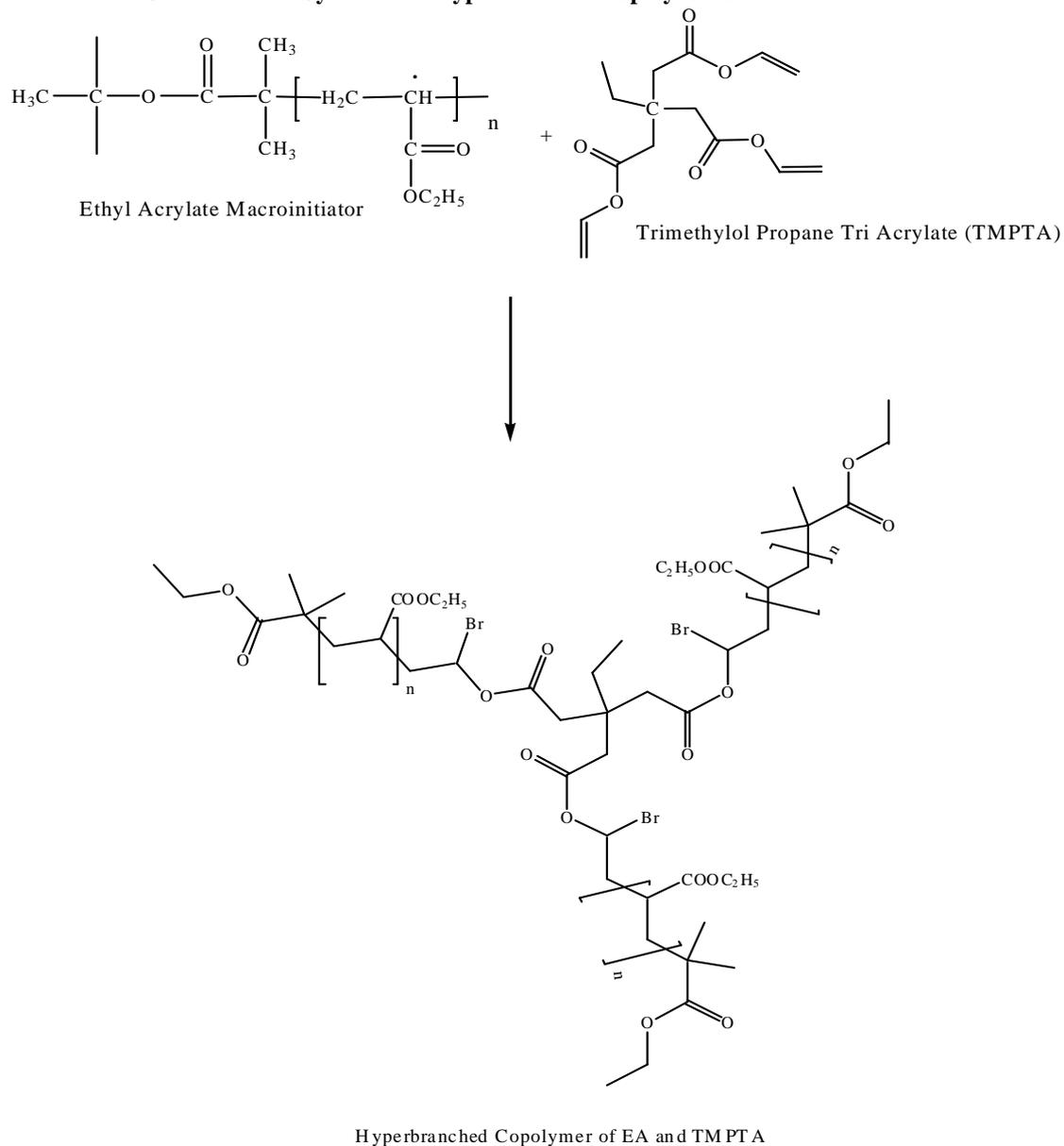


Figure No.1 (A): FTIR spectra of hyperbranched copolymer of EA and TMPTA having DP 5.

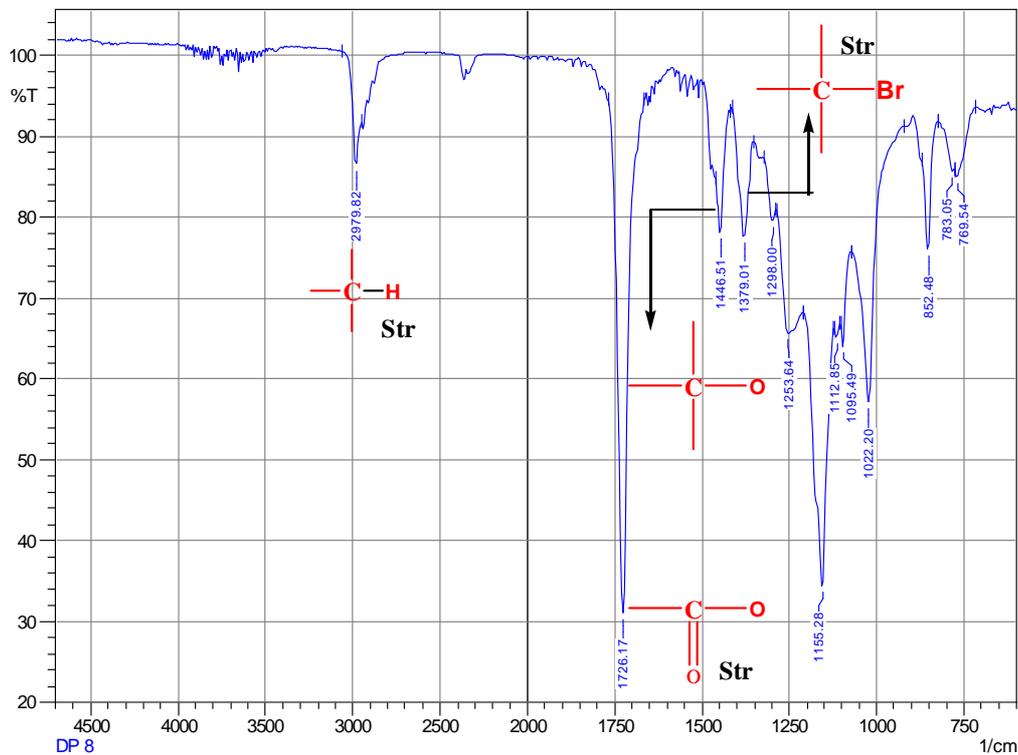


Figure No.1 (B): FTIR spectra of hyperbranched copolymer of EA and TMPTA having DP 10.

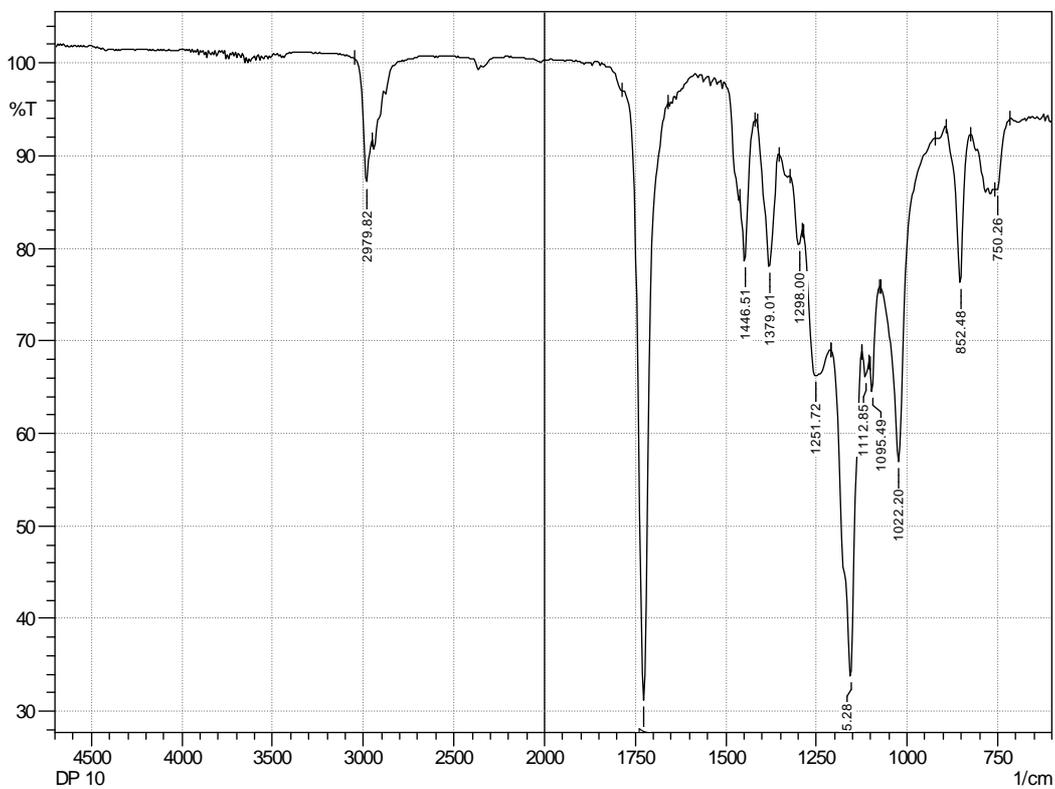


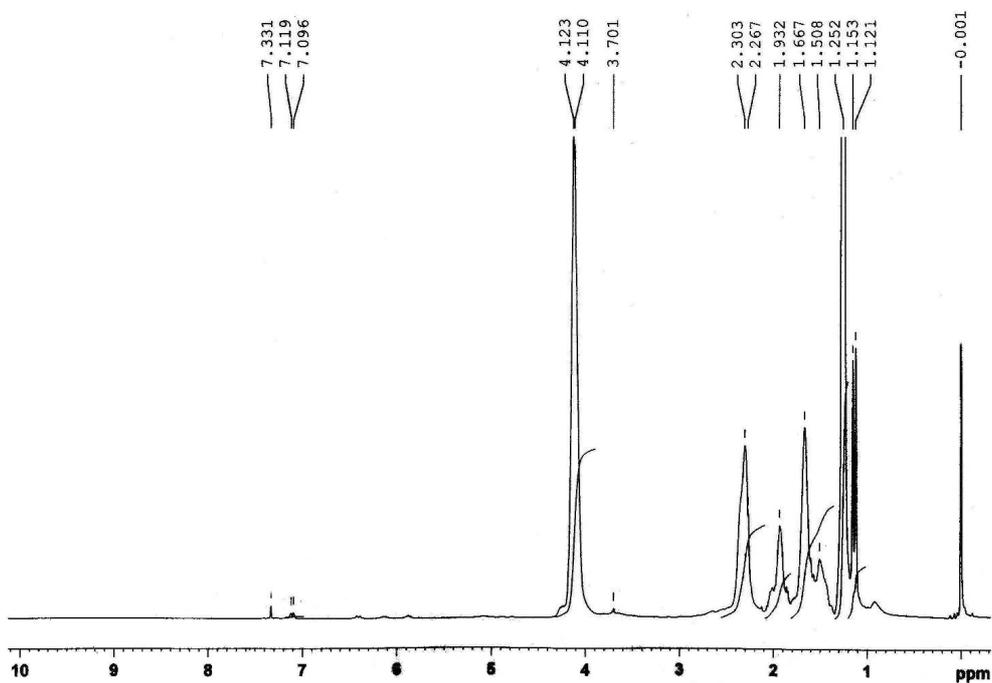
Figure No. 2:  $^1\text{H-NMR}$  Spectra of hyperbranched copolymer of EA and TMPTA

Figure No. 3: DSC thermogram of hyperbranched copolymer of degree of polymerization equal to 5.

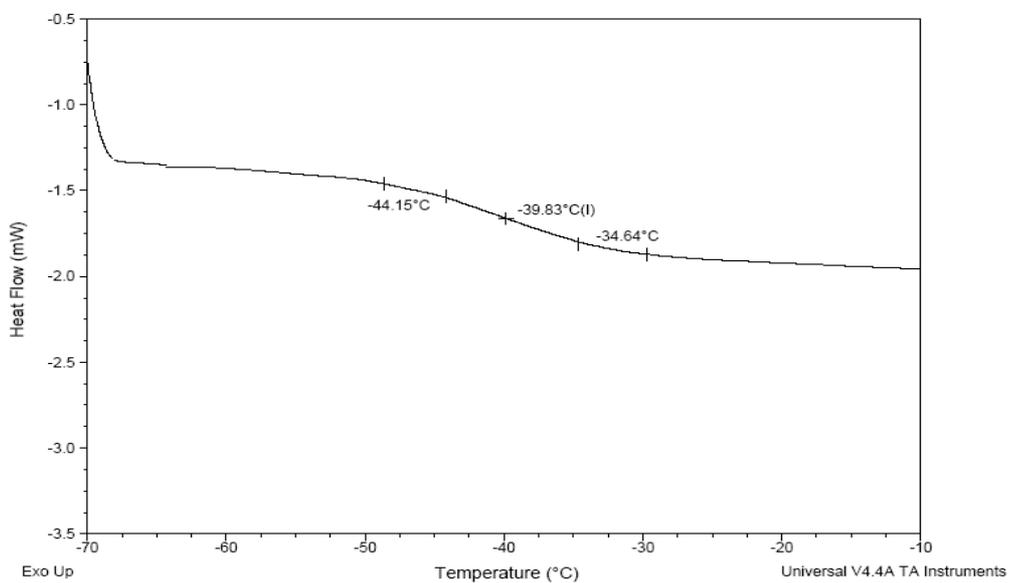


Figure No. 4: DSC thermogram of hyperbranched copolymer of degree of polymerization equal to 10.

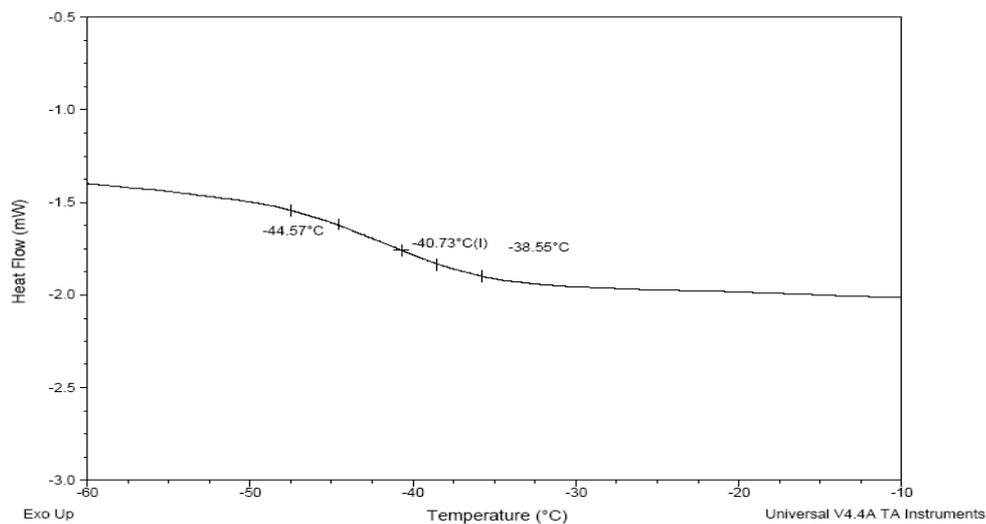


Figure No. 5: Graph of Viscosity Vs Shear Rate of hyperbranched copolymer for degree of polymerizations 5.

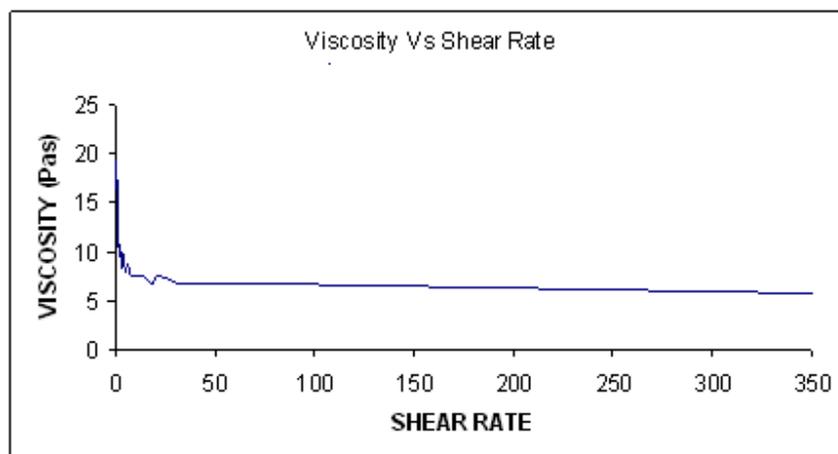


Figure No. 6: Graph of Viscosity Vs Shear Rate of hyperbranched copolymer for degree of polymerizations 10.

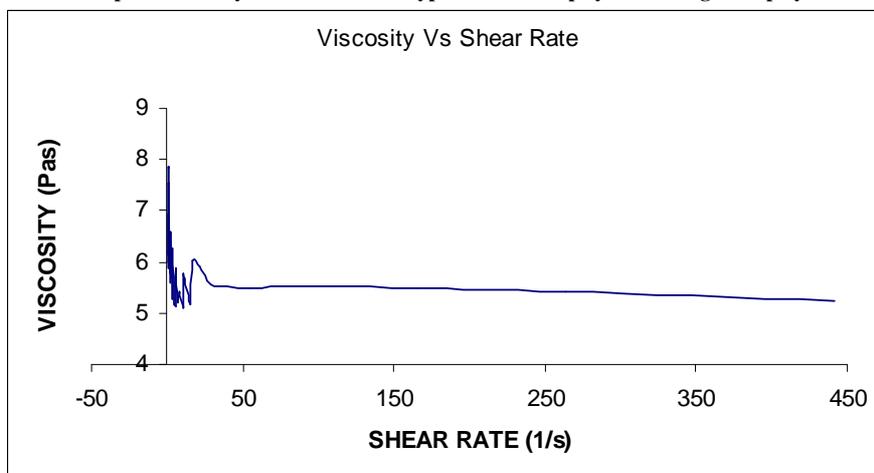


Figure No.7: Triple detection chromatography of the samples.

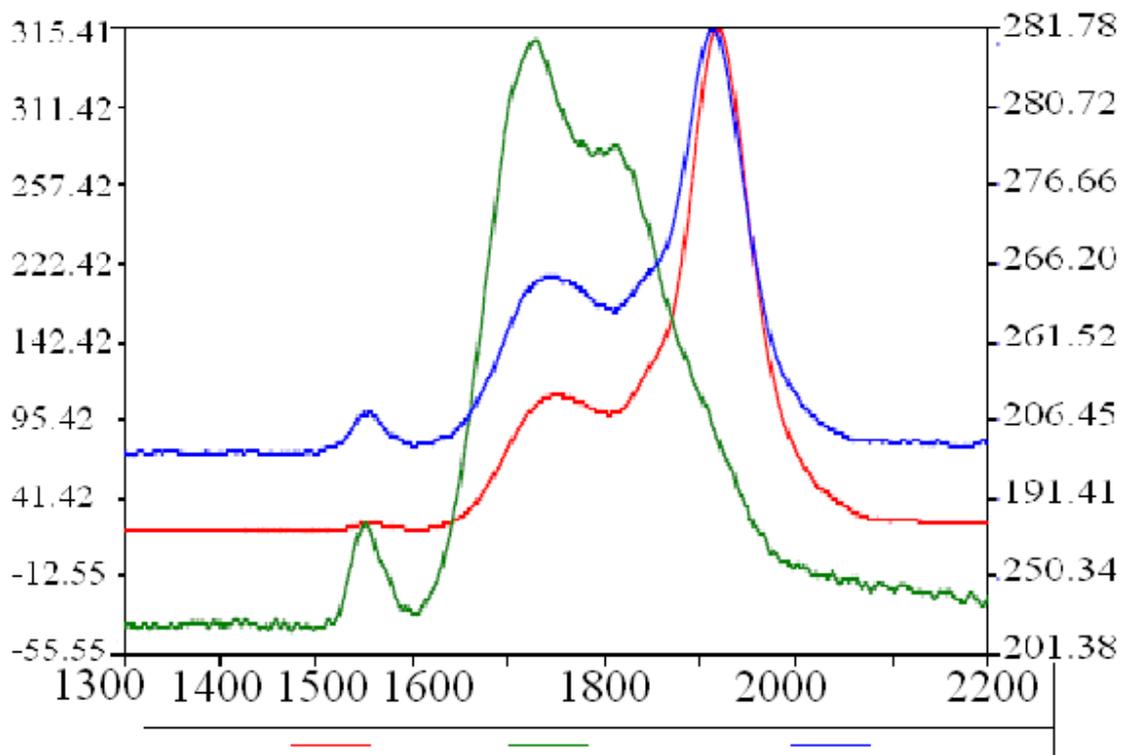


Figure No.8: the graph of viscosity Vs rpm.

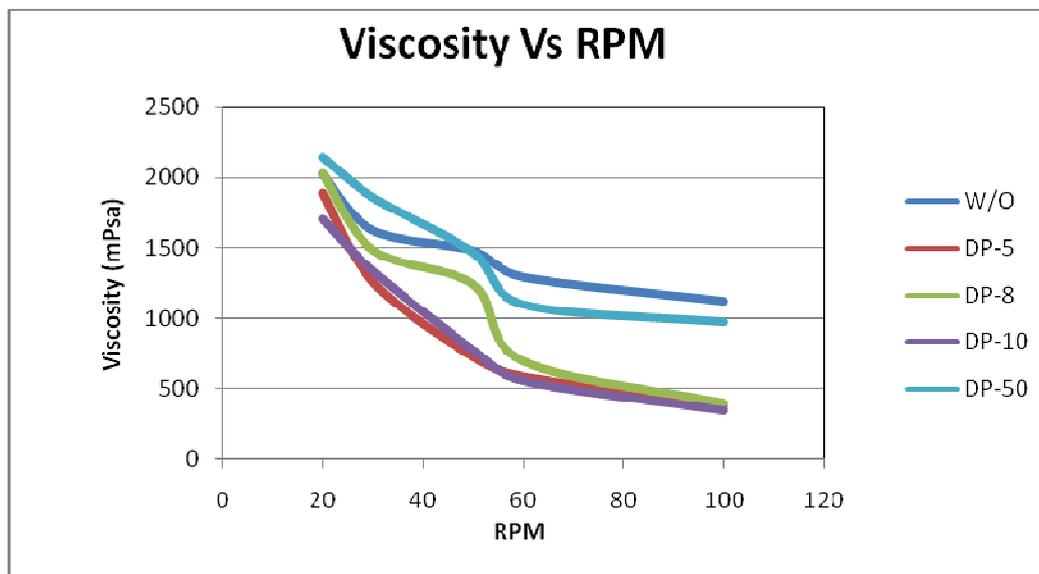


Figure No.9: Graph of % Reflectance Vs Wave Length for additive having DP – 5 in comparison with without additive

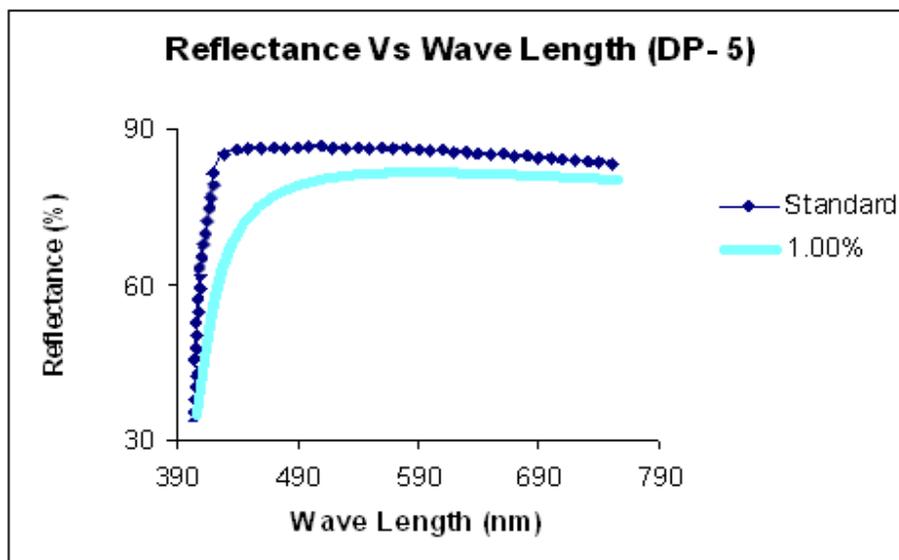


Figure No.10: Graph of % Reflectance Vs Wave Length for additive having DP – 8 in comparison with without additive

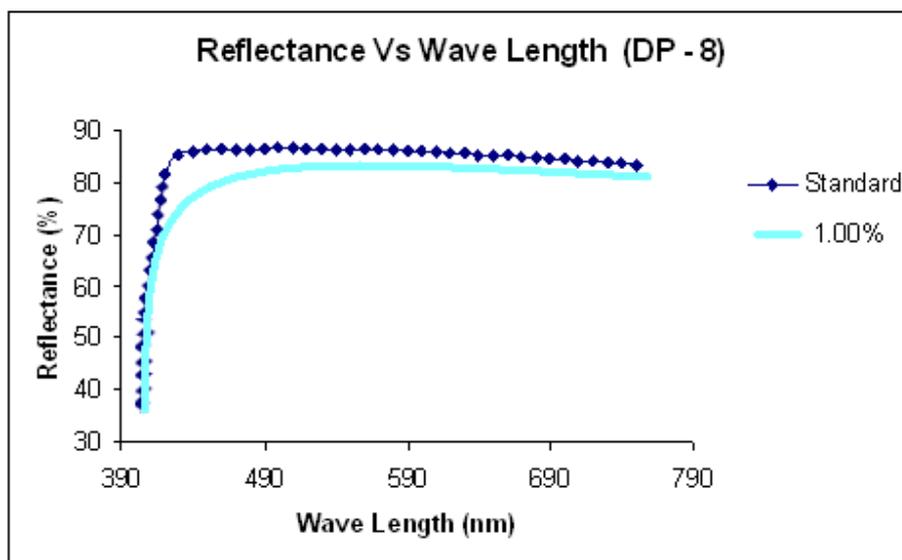
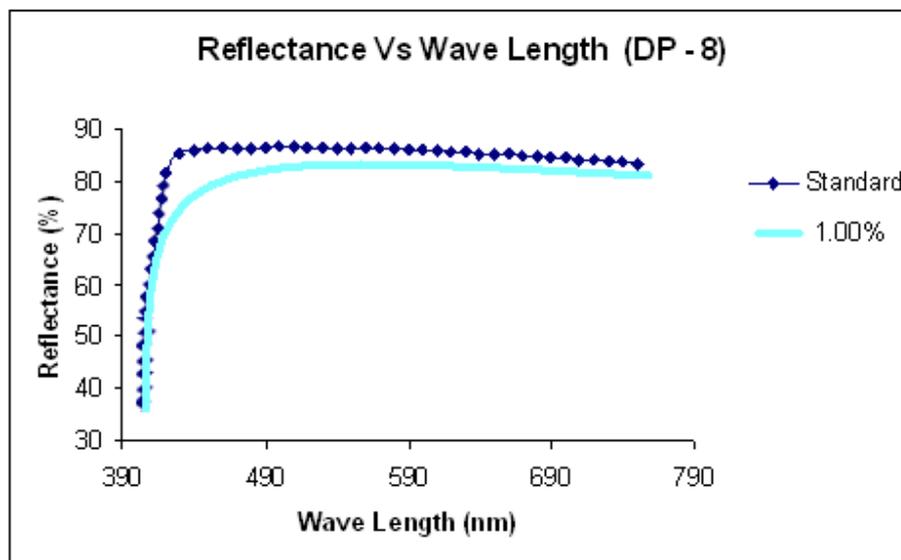


Figure No.11: Graph of % Reflectance Vs Wave Length for additive having DP – 10 in comparison with without additive



#### CONCLUSION

Hyperbranched polymer is well characterized by <sup>1</sup>HNMR, FTIR and SEC (Triple detection chromatography). This hyperbranched structure works as a rheological modifier for water based paints. The properties of the hyperbranched polymer with Dp-10 proved to be better compare to other polymers.

#### Acknowledgements

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#### REFERENCES

- [1] Kim, Y.H.; Webster, O.W. *J Am Chem Soc.*, **1990**, 112, 4592.
- [2] Gao, C.; Yan, D. *Prog. Polym. Sci.*, **2004**, 29, 183.
- [3] Voit, B. I.; Chimie, C. R. **2003**, 6, 821.
- [4] Matyjaszewski, K.; Xia, J. *Chemical Reviews*, **2001**, 101(9), 2921.
- [5] Kim, Y.H.; Webster, O.W. *J Am Chem Soc.*, **1990**, 112, 4592.
- [6] Hawker C.J, Lee R, Frechet JMJ. *J Am Chem Soc* **1991**, 113, 4583.
- [7] Malmstr M.E, Johansson M, Hult A. *Macromolecules* **1995**, 28, 1698
- [8] Schmaljohann, D.; Pötschke, P.; Haßler, R. *Macromolecules*, **1999**, 32, 6333.
- [9] *Prog. Poly. Sci.*, 25 (4) **2000**, 453-571
- [10] *Euro. Poly. J* 40 (7), **2004**, 1257-1281
- [11] *Encyclo. Material, Sci. & Tech.* **2008**, 3992-3997
- [12] *Prog. Poly. Sci.*, 29 (3), **2004**, 183-275
- [13] *Europ. Poly. J.*, 42 (8), **2006**, 1934-1938
- [14] Matyjaszewski, K.; Scott G.:Gaynor. *Macromolecules*, **1997**, 30(23), 7042.
- [15] Scott G.:Gaynor, Shane Edelman and Matyjaszewski, K.; *Macromolecules*, **1996**, 29(3), 1079.
- [16] Matyjaszewski, K.; Scott G.:Gaynor, Anthony Kulfan and Matthew Podwika, *Macromolecules*, **1997**, 30(17), 5192.
- [17] Matyjaszewski, K.; Peter J. Miller, Jeffrey Pyun, Guido Kickelbick, and Stephen Diamanti, *Macromolecules*, **1999**, 32(20), 6526.