# PREPARATION OF POLYSILOXANE NANO-PARTICLES CONTAINING SURFACE REACTIVE GROUPS FOR FURTHER FUNCTIONALIZATION

## A. M. ELFADLY, U. F. KANDIL, A. Y. EL-NAGGAR[*b],
## M. A. EBIED and R. M. ABDRABOU

Egyptian Petroleum Research Institute, Nasr, CAIRO, 11727, EGYPT
[a]Chemistry Department, Faculty of Science, Menofia University, SHIBEIN EL-KOM, EGYPT
[b]Chemistry Department, Faculty of Science, Taif University, TAIF, HAWIYAH, KSA

## ABSTRACT

Polysiloxane nano-particles containing surface reactive groups were synthesized and functionalized. The process involves two steps: emulsion co-polymerization of octamethylcyclo-tetrasiloxane and 1, 2, 3, 4-tetramethyl-1, 2, 3, 4-tetravinylcyclotetrasiloxane followed by thermal crosslinking. The crosslinking proceeds without consuming all the vinyl groups. The remaining vinyl groups contained in the nano-polymer were converted to epoxy groups using m-chloroper-benzoic acid, producing functionalized polysiloxane nano-particles. Characterization of nano polymeric siloxanes was carried out by TEM, TGA, GPC, FTIR, and $^{29}$Si and $^{13}$C solid state NMR. TEM images showed that the particles were globular with small particle size. TGA study of the nano-polymer indicated high thermal stability.

**Key words**: Polysiloxane, Nano-particles, Emulsion polymerization, Crosslinking, Epoxidation.

## INTRODUCTION

Polysiloxanes have been extensively used in various fields such as drug delivery systems[1], personal care products[2] and packing material for gas chromatography[3]. This can be attributed to their unique properties including excellent thermal stability, good hydrophobicity[4], good gas permeability, biocompatibility, climate resistance[5], a low glass transition temperature[6].

Microemulsion is a special heterophase system by which nanolatex particles in the size range from 5 to 100 nm are usually obtained[7]. Polysiloxane emulsions are simply

_____

[*]Author for correspondence; E-mail: aynaggar361@yahoo.com

prepared by ring opening polymerization (ROP) of cyclosiloxanes using either basic[2] or acidic catalysts[8-10]. A wide range of surfactants including anionic, cationic, or nonionic can be used to develop emulsion polymerization of siloxanes[11]. The microemulsion polymerization rate of siloxane with ionic surfactants is faster and produce higher molecular weight polymer than that of nonionic surfactants[12]. Dodecylbenzenesulfonic acid has attracted great attentions in siloxane emulsions, it can act as both emulsifier and catalyst[13].

It is a challenge to achieve crosslinked materials that allow further chemical surface modification with molecules or various functionalities[14]. For this reason the incorporation of vinyl group in silicones is very important, due to the ease with which this group can be functionalized[15] and/ or cross-linked[16]. Cross-linking of nano-latex stabilizes the structures against coalescence upon precipitation[17,18]. Crosslinking can leave some reactive groups on the surface of the particles, which are very versatile for both functionalization and post grafting leading to various applications[15,19].

To our knowledge, no attention has been paid to the preparation of polysiloxane nanoparticles. Encouraged by the afore-mentioned findings, we improve a good approach for the preparation, functionalization and characterization of polysiloxane nano-particles, as an important step to point out their applications.

# EXPERIMENTAL

## Materials

Dichlorodimethylsilane (DCMS) and dichloromethylvinylsilane (DCMVS) both were purchased from (Fluka; 99.0%) and were used as received. Diethylether (DEE) (Fluka; 99.0%) was used without further purification. 3-chloroperoxybenzoic acid (MCPBA) (Aldrich; 95%). Potassium peroxydisulfate (KPS) (Aldrich; 99.0%) was used as received. Dodecylbenzenesulfonic acid (DBSA) was purified by salting out. Deionized water was prepared in our lab. and tetramethyltetravinylcyclotetrasiloxane (DV4) were prepared as described previously[20].

## Instrumentation

**FTIR**: Perkin Elmer- Spectrum one, range 400-4000 cm^{-1}, number of scan 32 scan, resolution is 4, using neat KBr disk. The sample was mixed well with KBr and then made as a disk used for analysis.

**Solid state spectra:** These were obtained using Bruker MSL 300 spectrometer operating at 59 MHz for $^{29}$Si NMR and 75 MHz for $^{13}$C NMR the chemical shifts were measured relative to TMS. The spectra was obtained at room temperature.

**Measurement of molecular weight using gel permeation chromatography (GPC):** The instrument was equipped with pump model 515, RI detector model 2410 with a series of 4 columns styragel column, THF was used as the mobile phase with a rate of 1ml/min at $40^{o}$C, using polystyrene as the standard.

**High resolution transmission electron microscopy (HRTEM):** Measurements were conducted using a JEOL 2100 F TEM at an accelerating voltage of 200 kV. To prepare the TEM samples, a dilute particle–benzene colloidal mixture was ultrasonicated for 10 min and a drop of solution was placed on a carbon-coated Cu TEM grid.

**Thermogravimetric analysis:** Measurement was conducted on TA Instruments SDTQ 600 simultaneous TGA-DSC thermogravimetric analyzer. A known amount of sample was loaded and evenly spread on the alumina microcrucible. The samples were heated under nitrogen at temperature ranging from 50 to $800^{o}$C, at $10^{o}$C min$^{-1}$.

## Preparation of octamethylcyclotetrasiloxane (D4)

To 300 mL distilled water, cooled in an ice bath, a solution of dichlorodimethyl-silane (100 mL) and diethyl ether (100 mL) was added drop-wisely by a means of addition funnel while water is vigorously stirred. The temperature of the reaction was maintained less than $10^{o}$C. After complete addition of DCDMS, the reaction was allowed to take place for an additional hour. The organic layer was separated using a separating funnel. After separation the organic layer was washed several times with a dilute solution of sodium bicarbonate (NaHCO$_3$) (to remove HCl) then it was washed with distilled water and dried over anhydrous magnesium sulfate (MgSO$_4$). Ether was evaporated by rotary evaporator until we get a constant weight.

## Preparation of tetramethyltetravinylcyclotetrasiloxane (D$^{V}$4)

200 mL distilled water was charged in a three-necked flask equipped with a reflux condenser, thermometer and a stirrer immersed in an ice bath. A solution of vinylmethyl dichlorosilane (50 mL) and diethylether (70 mL) was added to the above mentioned mixture very slowly so that the reaction temperature does not exceed $5^{o}$C. After complete addition of the silane, the reaction was stirred for 1.5 hr. The ethereal layer was separated and washed

with dilute ($NaHCO_3$) solution and then with distilled water. It was dried over anhydrous ($MgSO_4$) and then ether was evaporated by rotary evaporator when an oily product was obtained.

## Preparation of polysiloxane nanolatex

Polysiloxane nanolatex was prepared by emulsion copolymerization of D4 and $D^V4$ as follows: In a 200 mL beaker 10 g of D4 and 30 g of $D^V4$ were mixed and agitated very well with 4 g of DBSA and 70 mL deionized water and then transferred to the addition funnel. In 500 mL three-necked glass flask equipped with a reflux condenser, thermometer and a stirrer, 14 g of DBSA were dissolved in 100 mL deionized water. The flask was heated on an oil bath to keep the temperature during the reaction around 80-90°C. Addition funnel was connected to the flask and the monomer was allowed to beadded very slowly over 2 hr. When the addition was complete, the reaction was stirred for additional 5 hr.

A sample was withdrawn from the reaction medium and neutralized with a dilute solution of NaOH to stop the catalyst. This sample was used to measure the Molecular weight of the polymer by GPC before crosslinking. To stabilize the nanolatex, crosslinking of the nanolatex was developed by the addition of KPS (1 wt. % of the reaction mixture) to the emulsion after purging with $N_2$ for 15 min. The reaction mixture was stirred for 5 hr under $N_2$. The polymer was precipitated in excess of methanol, filtered and washed several times with methanol. The polymer finally dried in vacuum oven at 50°C overnight.
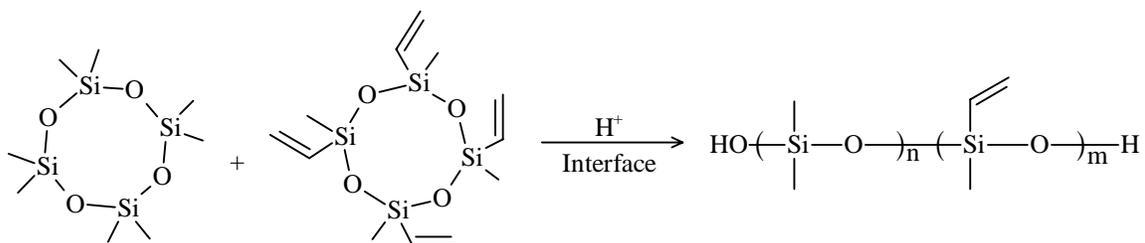
## Epoxidation

Polysiloxane nanoparticles (2 g) were dispersed in 70 mL toluene in a flask and purged with nitrogen for 10 min. then 4 g of m-chloroperbenzoic acid dissolved in toluene was added to the flask. The reaction was stirred at 60°C for 5 hr. The reaction was stopped by the addition of methanol. The epoxy-containing polymer obtained was filtered, washed with an excess amount of methanol and dried in vacuum at 50°C overnight.

## RESULTS AND DISCUSSION

### Microemulsion formation

To obtain a stable microemulsion, a large amount of surfactants should be used[21]. The minimum ratio of surfactant to polysiloxaneneeded to generate stable and clear aqueous microemulsion is 0.15 weight ratios as observed by Graiver and Tanaka[22]. However, larger quantities of surfactants produce smaller droplet size. The main reaction of cyclosiloxanes in

emulsion is (ROP) of cyclosiloxane monomers which was found to take place at interface. This gives DBSA the advantage that it acts not only as a surfactant but also as initiator (inisurf) for the ROP[13]. Based on these observations and previous cationic cyclosiloxane polymerization studies, a reaction scheme can be proposed.



**Scheme 1: Cationic ROP of D4 and D4$^V$ in emulsion**

## Crosslinking of nanolatex

Although crosslinking of polysiloxane emulsions was reported before using trifunctional alkoxysilanes[23] and trichlorosilane[24], the current crosslinking give a chance for preparing nano-particles containing surface reactive groups available for further functionalization. Crosslinking was effectively performed using peroxide. When KPS is heated to its decomposition temperature, free radicals readily evolved. The free radicals attack double bonds, permitting rapid and efficient cross-linking reactions to occur[25]. KPS develops crosslinking via both methyl and vinyl groups, forming mostly propylene and butylene bridges between polymer chains[26], a few ethylene bridges may also be formed[25].

## Characterization

## a) Spectroscopic analysis

The structure of the synthesized compounds were well characterized from their satisfactory spectral (IR, NMR) studies.

The IR spectrum of the prepared polysiloxane nanoparticles displayed bond characteristic of vinyl group at 1623 cm$^{-1}$, and three peaks at 1020-1098 cm$^{-1}$, 1262 cm$^{-1}$, and 2900 cm$^{-1}$ attributed to the stretching vibration mode of Si-O-Si, Si-CH$_3$ and CH$_3$ respectively. A look at solid state $^{29}$Si NMR (Fig. 1) showed a clear peak located at -23 ppm that related to a new side crosslink structure (silicon bonded to propylene in the crosslinked polymer)[27]. In addition, the two signals at -22 and -35 ppm are assigned to silmethyl and

silvinyl, respectively. Peak at -35 ppm indicates the presence of residual double bonds. Thus, it is reasonable to conclude that the presence of active vinyl group in the prepared nano-polymer after cross-linking is ready for further modification. Another evidence comes from the solid state $^{13}$C NMR (Fig. 2) since three peaks appeared at 0.2, 14.4 and 29.9 ppm corresponding to methyl and two methylene carbon groups suggesting cross-linking occurred via both methyl and vinyl groups that lead to the formation of mostly propylene and butylene bridges. While the two signals appeared at 133 and 137 ppm are attributed to the two carbons of vinyl group.



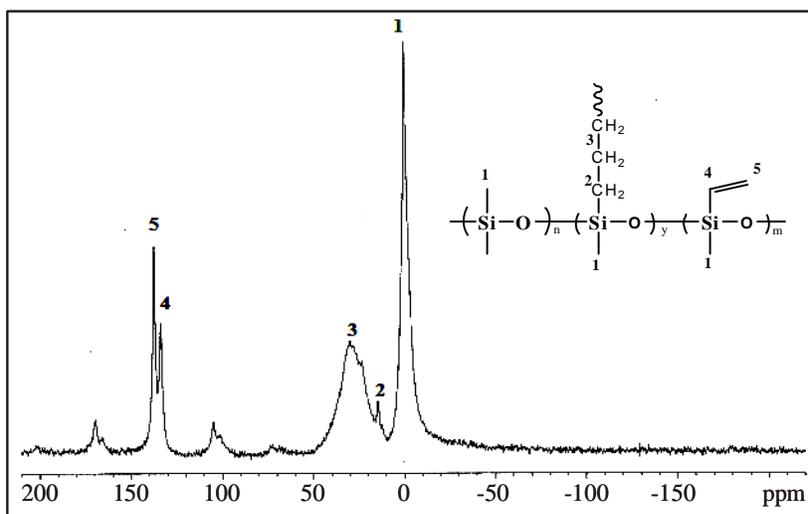**Fig. 1: Solid state $^{29}$Si NMR of nanopolysiloxane**



**Fig. 2: Solid state $^{13}$C NMR of nanopolysiloxane**

**b) Molecular weight of polymer**

The average molecular weight of the polymer before cross linking was conducted using GPC. GPC results shows that the polymer has MW of about 66000 with polydispersity of 1.29. This relatively high molecular weight is expected from cationic ROP of cyclosiloxane[10].

**c) Thermal analysis**

The thermal stability of the prepared polysiloxane nanoparticles was studied by TGA. Polysiloxanes have good thermal stabilities which could be attributed to high bond dissociation energy of Si-O bond[28]. The thermal stability of polysiloxane is enhanced by crosslinking[29]. The thermogravimetric studies, presented in (Fig. 3), revealed that nanopolysiloxane undergo thermal decomposition at 450$^{\circ}$C and at 485$^{\circ}$C, which is corresponding to weight loss of 5% and 10%, respectively. The residual mass (char yield) at 800$^{\circ}$C is 44.8 %. It is worth mentioning that the thermal stability of the prepared nanopolysiloxane is apparently greater than that obtained for ladder like polysiloxane[30].
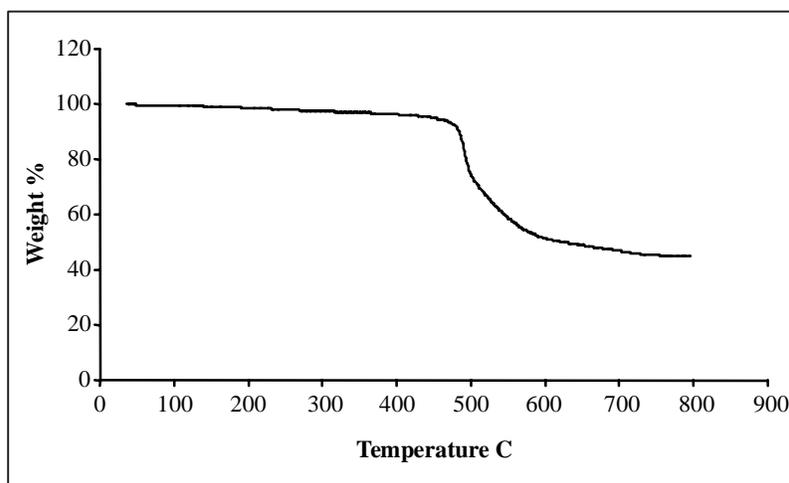


**Fig. 3: TGA of nanopolysiloxane**

**d) Morphology of nanosilicone**

TEM was used to investigate the shape and the size of polymer nanoparticles. Figure (4) shows TEM photograph of polysiloxane nano-particles. From TEM image we can conclude that the particles are globular, with a diameter ranged between 10 nm and 20 nm.

Particles with a diameter greater than 20 nm could be attributed to the coalescence of two or more droplets during the crosslinking, precipitation and drying processes.
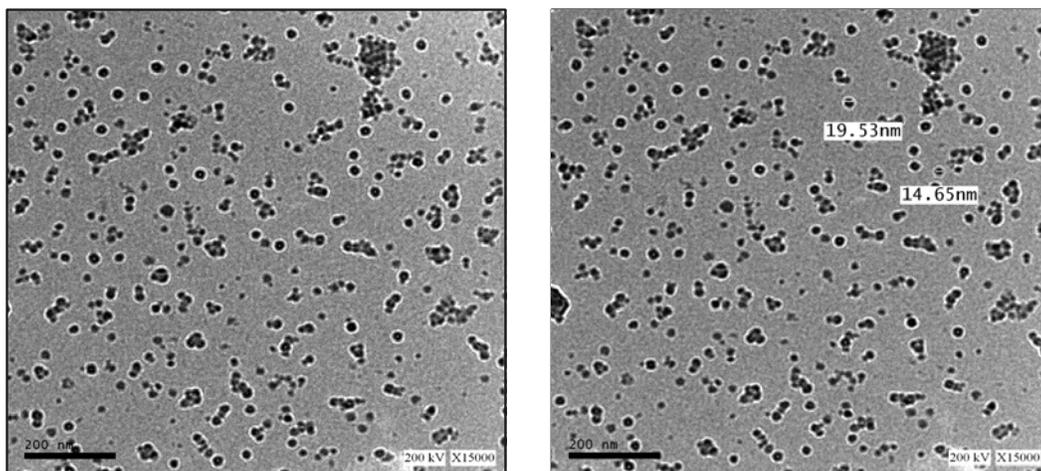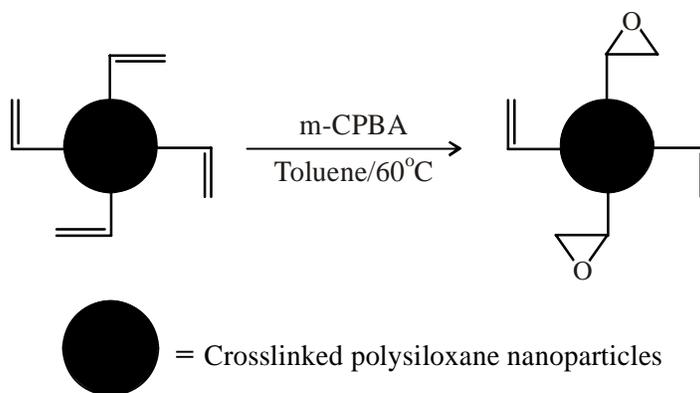


**Fig. 4: TEM of polysiloxane nano-particles**

**Epoxidation**

To our knowledge polysiloxane nano-particles have not been epoxidized before. However epoxidized polysiloxanes already known before[31]. The epoxidation of poly (dimethyl-*co*-methyl vinyl) siloxane was conducted at 60°C in toluene for 5 hr. using *m*-chloroperbenzoic acid as shown in Scheme 2. Figures 5 and 6 show the $^{29}$Si NMR and the $^{13}$C NMR of epoxidized polymer.



**Scheme 2: Epoxidation of polysiloxane nanoparticles**
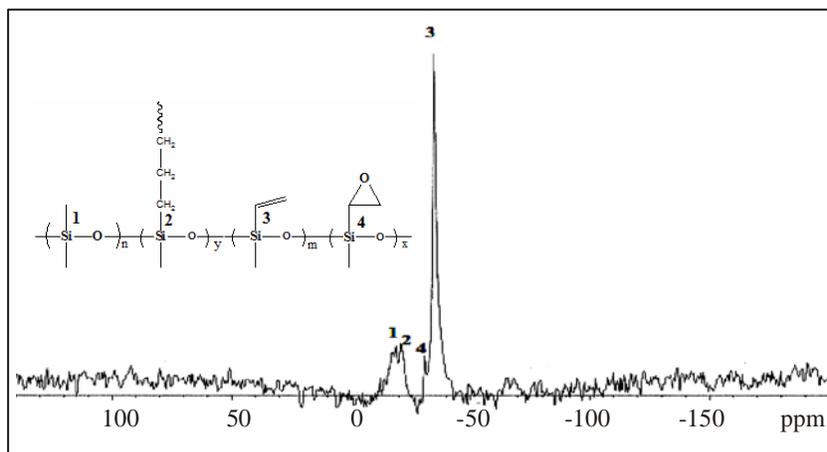
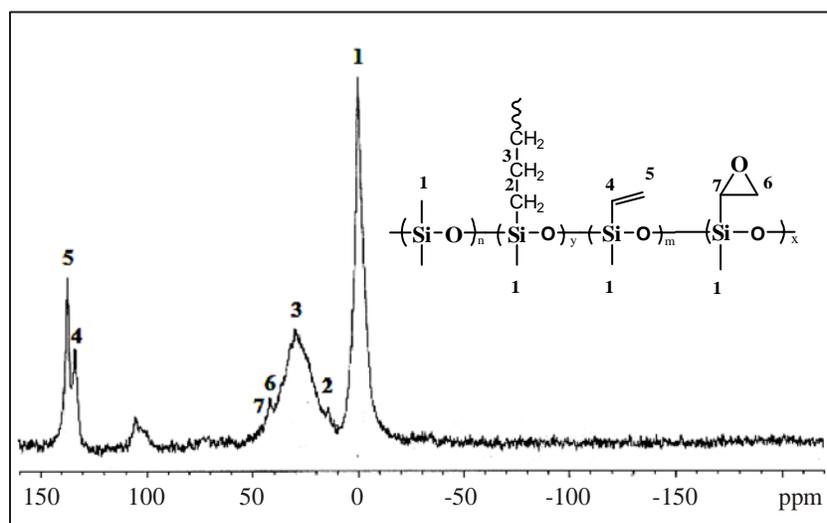**Fig. 5: Solid state $^{29}$Si NM Rof Epoxidized nanopolysiloxane**



**Fig. 6: Solid state $^{13}$C NMRof Epoxidized nanopolysiloxane**

The appearance of a new peak at -29.8 ppm[31] which is assigned to oxirane ring attached to silicon atom proves the epoxidation of double bonds in polymer. One can notice a strong peak at -34 ppm coincide with the existence of double bonds remaining after this epoxidation. The same conclusion can be seen from $^{13}$C, where the appearance of peak at 41.8 ppm[31] indicates the formation of epoxy group, the peaks at 133-137 ppm shows that some double bonds still remain.

# CONCLUSION

Microemulsion polymerization of cyclosiloxane monomers was utilized in the preparation of polysiloxane nanoparticles. The preparation was carried out by ROP of cyclic monomers using DBSA as inisurf. The introduction of active group was allowed by using monomer containing vinyl groups. The active groups were used to stabilize nanolatex through crosslinking. After crosslinking, the remaining vinyl groups are a versatile for functionalization to introduce epoxy group to the nanopolymer. The chemical structure of the prepared polymers was elucidated by FTIR, ^{13}C NMR, ^{29}Si NMR that give a detailed information concerning the vinyl group and oxirane ring as indicated by the chemical shifts. The polymer shows high thermal stability as monitored by TGA. Particles morphology was studied by TEM showing that the particles are globular with small sizes.

# REFERENCES

1.  A. Mashak and A. Rahimi, Iran. Polym. J., **18**, 279-295 (2009).

2.  M. Barrere, F. Ganachaud, D. Bendejacq, M. A. Dourges, C. Maitre and P. Hemery, Polymer, **42**, 7239-7246 (2001).

3.  J. D. Zeeuw and J. Luong, Trends Anal. Chem., **21**, 594-607 (2002).

4.  M. Ines and S. Urska, Polymer, **52**, 1234-1240 (2011).

5.  F. Shengyu, Z. Jie, W. Dake, W. Mingyan and Y. Zhaotan, J. Appl. Polym. Sci., **94**, 110-115 (2004).

6.  M. W. Fu, C. W. Chi and Y. W. Yung, J. Appl. Electrochem., **39**, 253-260 (2009).

7.  L. Shiyong, D. H. Kevin and W. K. Eric, Macromolecules, **39**, 4345-4350 (2006).

8.  A. De Gunzbourg, S. Maisonnier, J. C. Favier, C. Maître, M. Masure and P. Hémery Macromol. Symp., **132**, 359-370 (1998).

9.  D. E. Findlay and D. R. Weyenberg, US Patent, **3**, 294, 725 (1966).

10. S. Maisonnier, J. C. Favier, M. Masure and P. Hémery Polym. Int., **48**, 159-164 (1999).

11. D. Graiver and O. Tanaka US Patent, **5**, 817, 714 (1998).

12. D. Zhang, X. Jiang and C. Yang, J. Appl. Polym. Sci., **89**, 3587-3593 (2003).

13. S. Jiang, T. Qiu and X. Li, Polymer, **51**, 4087-4094 (2010).

14.   T. Thami, G. Nasr, H. Bestal, A. V. Lee and B. Bresson, J. Polym. Sci. Pol. Chem., **46**, 3546-3562 (2008).

15.   I.  Kim, React. Funct. Polym., **49**, 197-204 (2001).

16.   H. Jacob, S. Bengt and P. Maria, Polym. Test, **22**, 253-257 (2003).

17.   A. Guo, G. Liu and J. Tao, Macromolecules, **29**, 2487-2493 (1996).

18.   V. Butun, A. B. Lowe, N. C. Billingham and S. P. Armes, J. Am. Chem. Soc., **121**, 4288-4289 (1999).

19.   J. Bauer, N. Husing and G. Kickelbick, J. Polym. Sci. Pol. Chem., **42**, 3975-3985 (2004).

20.   W. Patnode and D. F. Wilcock, J. Am. Chem. Soc., **68**, 358-363 (1946).

21.   Y. Q. Zhuang, X. Ke, X. L. Zhan and Z. H. Luo, Powder Technol., **201**, 146-152 (2010).

22.   D. Graiver and O. Tanaka, US Patent, **4**, 999, 398 (1991).

23.   A. Bey, US Patent, **4**, 424, 297 (1984).

24.   N. Terae, and A. Abe, US Patent, **4**, 465, 849 (1984).

25.   S. R. Lipsky and W. J. Mcmurray, J. Chromatogra., **239**, 61-69 (1982).

26.   M. L. Dunham, D. L. Bailey and R. Y. Mixer, Ind. Eng. Chem., **49**, 1373-1376 (1957).

27.   D. J. T. Hill, C. M. L. Preston and A. K. Whittaker, Polymer, **43**, 1051-1059 (2002).

28.   S. Ahmad, A. P. Gupta, E. Sharmin, M. Alam and S. K. Pandey, Prog. Org. Coat., **54**, 248-255 (2005).

29.   Y. Han, J. Zhang, L. Shi, S. Qi, J. Cheng and R. Jin, Polym. Degrad. Stabil., **93**, 242-251 (2008).

30.   Y. Lin, K. P. Pramoda, C. He, W. Y. Chen and T. S. Chung, J. Polym. Sci. Pol. Chem., **39**, 2215-2222 (2001).

31.   J. Bauer, N. Husing and G. Kickelbick, J. Polym. Sci. Pol. Chem., **40**, 1539-1551 (2002).