

Research Article

Synthesis and Structure of Poly(methyl methacrylate) (PMMA) Nanoparticles in the Presence of Various Surfactants

Asma Khalaf Alshamari¹ and Wafaa Mahmoud Sayed*²

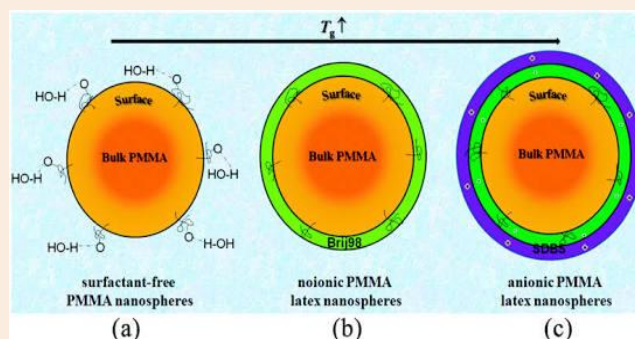
¹Department of Chemistry, University of Hail, Hail, Saudi Arabia

²Petrochemical Department, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

Abstract

Polymerization of methyl methacrylate (MMA) nanoparticles will be carried out in the presence of different surfactants. In this study, anionic (SDS), nonionic (NPE), and cationic (CTAB) micelles will be used as polymerization media to produce poly (methyl methacrylate) (PMMA) nanoparticles. The concentration of the surfactants during the emulsion polymerization affects both, the size of the formed PMMA nanoparticles and their electrical surface state. The structure of the obtained PMMA nanoparticle will be studied through transmission electron microscopy (TEM), thermo gravimetric analysis (TGA), fourier transform infrared (FTIR) spectra, X-ray diffraction (XRD) and electrical properties.

The PMMA nanoparticles revealed enhanced conductivity compared to conventional bulk PMMA. The results revealed that the PMMA nanoparticles retarded thermal decomposition and enhanced the conductivities compared with pristine PMMA nanoparticles.



Keywords: Poly (methyl methacrylate), Nanocomposites, Polymerization, surfactants

*Correspondence

Wafaa Mahmoud Sayed

Email: wafaamahmoudsayed@hotmail.com

Introduction

The importance of polymers is mainly because polymers are still regarded as a cheap alternative materials that are manufactured easily^[1]. Polymer nanoparticles have attracted the interest of many research groups and have been utilized in an increasing number of fields during the last decades^[2].

Polymer nanomaterials have received much attention due to their special properties arising from their small size. Owing to the high surface/volume ratio of the small particles, the percentage of molecules or atoms on the surface is greatly increased. These properties are desirable for applications in various fields, such as: Drug delivery^[3-6], sensors^[7,8], molecular gels^[9,10], semiconductors^[11], catalysts^[12,13], environmental applications^[14], and industrial applications^[15].

A variety of methods have been reported to prepare polymer nanoparticles, such as: Solvent evaporation^[16], molecular assembly^[17], template chemistry^[18], dendrimer polymerization^[19], mechanical pulverization^[20], microemulsion polymerization^[21], and miniemulsion polymerization^[22].

Intrinsically conductive polymers (ICPs) are considered as attractive subject of research because of their potential applications in multidisciplinary areas, such as: Electrical, electronics, thermoelectric, electrochemical, electrorheological, chemical, membrane, and sensor applications^[23-26]. A useful approach to overcoming some of the

physical and chemical limitations, including the processability and mechanical and thermochemical stabilities of ICPs, involves the combination of these materials with other well-known nonconducting polymers, such as: Poly(vinyl alcohol), polystyrene, poly(methyl methacrylate) (PMMA), and poly(vinyl acetate)^[27].

Poly(methyl methacrylate) (PMMA) is one of the important transparent thermoplastic plastics, which has been utilized to make windows, lenses, and other optical devices^[28] and used to improve the mechanical properties and processability of PANI. PMMA is chosen as a dielectric matrix because of its high transparency in the visible spectral range, which is important for optoelectronics, sensors, and smart-window applications^[29]. Recently, several researchers synthesized polymer nanoparticles using microemulsion polymerization^[30-34]

Using differential microemulsion polymerization, PMMA particles can be controllably synthesized with respect to their nanosize and molecular weight, as well as polymer chain number in the particles.

In this article, we report the fabrication of PMMA nanostructures with microemulsion polymerization. The size of the PMMA nanoparticle was controlled as a function of different surfactants (anionic, cationic, and nonionic). In addition, we will investigate the conductivity of PMMA nanoparticles as dependent on the type of surfactant.

Experimental:

Materials and reagents:

MMA (Aldrich, Steinheim, Germany), potassium peroxydisulfate (KPS), sodium dodecyl sulfate (SDS; 99%), nonyl phenol ethoxylate (NPE), and cetyltrimethyl ammonium bromide (CTAB) (was obtained from Aldrich Chemical Co.)

Measurements:

Fourier transform infrared (FTIR) spectra:

The FTIR spectra of the synthesized PMMA were recorded using Nicoletis-10 FTIR Spectrometer.

Transmission electron microscopy (TEM):

The microstructures of the synthesized PMMA were examined by TEM (Japan) on a JEOL JEM- 2100 (Japan) at an accelerating voltage of 120 kV.

X-ray diffraction (XRD):

The XRD patterns of the PMMA nanoparticles synthesized with different types of surfactants (anionic, nonionic, and cationic) were recorded using Pan Analytical model X'Pert pro diffractometer with Cu K α ($\lambda = 1.54060 \text{ \AA}$) incident radiation. The XRD peaks were recorded in the 2θ range of 10° – 80°

Conductivity measurement:

The PMMA samples were pressed into pellets in a manual hydraulic Press - 15 tons (model GS15011 – Atlas Manual 15T). We determined the bulk conductivity of the different polymer samples by pressing them into pellets with thickness ranging between 2.4 and 4.4 mm.

The conductivity measurements were carried out by a four-probe technique recorded by a Keithley Electrometer HiGH /Resistancemeter (model 6517A). The pellets used in this measurement were placed between two copper electrodes, which were connected to the two terminals of the Keithley electrometer and the data were recorded at room temperature.

Thermogravimetric analysis (TGA) measurements:

TGA of the synthesized PMMA was carried out on a TA Instruments SDTQ 600 V20.5 Build 15 simultaneous (United States) TGA–differential scanning calorimetry thermogravimetric analyzer. The samples were heated under a nitrogen flow (100 mL/min) from 50 to 500°C at a rate of 20°C/min.

Synthesis of the PMMA nanoparticles

PMMA nanoparticles will be synthesized through differential microemulsion polymerization by a semi-batch operation. Potassium persulfate (KPS) will be used as the initiator and sodium dodecyl sulfate (SDS), nonyl phenol ethoxylate (NPE), and cetyltrimethyl ammonium bromide (CTAB) as the surfactants. KPS, surfactant and deionized water will be put into a three-neck round-bottom flask (250 ml) equipped with magnetic stirrer, reflux condenser, and thermometer. After the temperature will be raised to 75°C, the monomer will be added in a differential manner (continuously addition in very small drops) for about 1h. Afterwards, the reaction temperature will be kept at 80–85°C for an additional hour before a cooling operation applied.

Separation of polymer samples for characterization

The resultant polymer was precipitated using methanol and was separated by a vacuum filtration technique. The surfactant and initiator were washed off the particles three times with a sufficient amount of warm de-ionized water, polymer was dried in oven at 80°C.

Several PMMA nanoparticles were synthesized with different types of surfactants (SDS, NPE, and CTAB) to investigate the morphology, conductivity, and TGA. For comparative purposes, PMMA without surfactants was also synthesized under similar conditions.

Results and Discussion

First, a micellar solution was prepared by the dissolution of the surfactant in distilled water with the concentration over its cmc. It has been well established that surfactants will aggregate spontaneously to form micelles when the concentration is over their cmc. Because of the presence of the hydrophobic micellar core and hydrophilic interface, these micelles are capable of dissolving water-insoluble substances.^[35]

A certain amount of MMA is added to the solution to be loaded onto the micelles, these micelles may serve as templates to orient and organize the MMA molecules in the solution. The orientation or organization of MMA molecules in the micelle solutions may have affected the regioselectivity of the reaction. Different types of surfactants with different molecular structures were selected to form the micelle templates for the polymerization of MMA. The difference in the behavior of the polymerization of MMA in various micelle solutions could be explained by the variation of the local environment formed by different surfactants. In all of these micelle solutions, hydrophobic cores were formed; however, the hydrophilic interfaces of the micelles were quite different because of the differences in the head-group structure of the surfactants.

The head group of NPE was polyoxyethylene, with nine repeat units without any charge. Therefore, a neutral hydrophilic interface was formed around the NPE micelles in the solution. The long ethylene oxide chain in NPE effectively hindered the sulfate ions (oxidant, KPS) from attacking the MMA in the micelles.

Thus, the formation of PMMA particles in NPE micelles was very slow because the disulfate ions should have diffused through the films formed by the ethylene oxide chains to initiate polymerization. No electrostatic interactions between the head group of NPE and other species were expected at the hydrophilic interface other micelles. On the other hand, if a positively charged hydrophilic region in the CTAB micelle solution was formed, anionic species such as OH would have been likely attracted in this region through electrostatic interaction. When oxidant KPS was added to the reaction system, the polymerization took place at nanoscale micelles and was then followed by PMMA growth. The micelles formed by surfactants such as SDS had negatively charged interfaces in the solution. This negative charge of the micellar surface retarded the approach of disulfate ions into ions; this resulted in a slower reaction rate in the SDS micellar solution compared to that in the bulk aqueous solution.

1. FTIR spectroscopy

(Figure 1) presents the FTIR spectra of the prepared PMMA nanoparticles. The main characteristic bands of PMMA were assigned as follows:

The band at about 753 cm^{-1} is assigned to out of plane OH bending. The band at around 980 cm^{-1} is the characteristic absorption vibration of PMMA. Stretching vibration frequency of (---CH_3) appears at wave numbers of 2951 cm^{-1} and 2850 cm^{-1} , and the bending vibration frequency of (---CH_3) is at a wave number of 1384 cm^{-1} . The wave number

1730 cm^{-1} corresponds to the stretching vibration frequency of (—C=O). The wave number 1150 cm^{-1} represents the stretching vibration frequency of (—C—O). Our samples contain water, which is shown in the marked area in Figure (from 3200 to 3750 cm^{-1}). Thus, it was confirmed that our product is the PMMA.

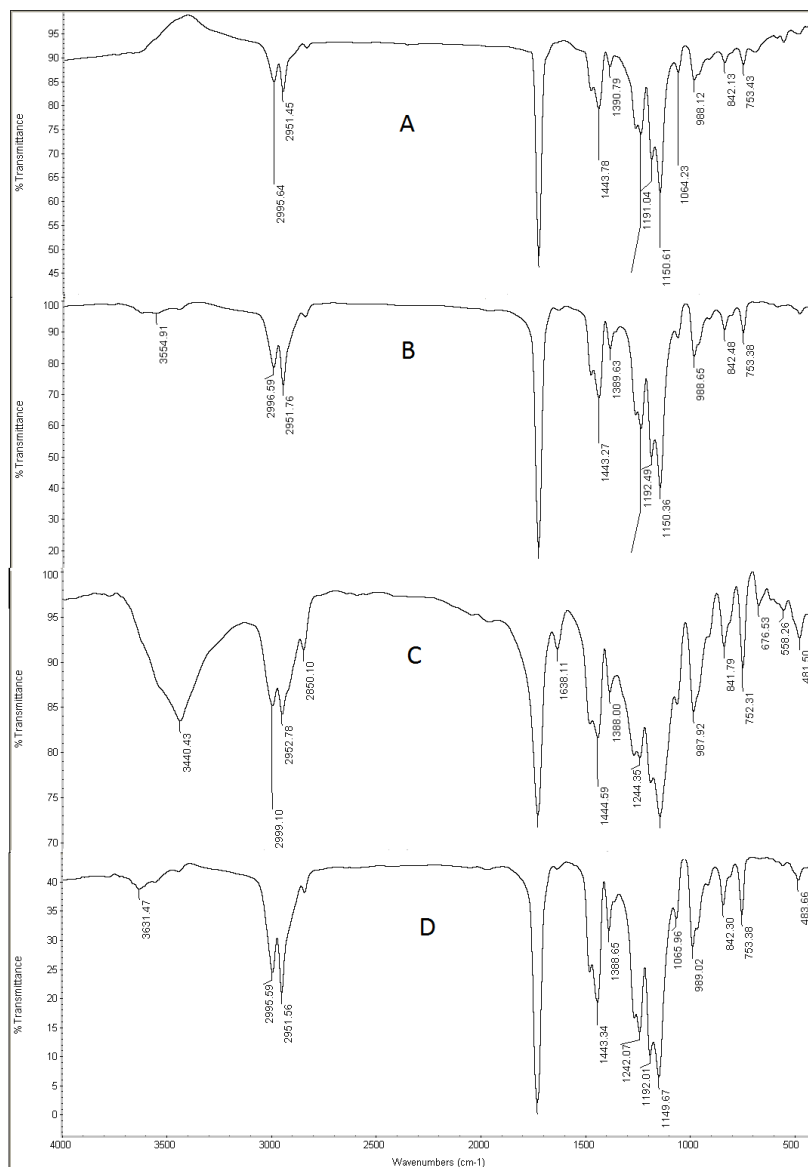


Figure 1 FTIR spectra of PMMA synthesized in (a) cationic, (b) anionic, and (c) nonionic surfactants and (d) without surfactants

2. TEM:

The surfactant is one of the key components in microemulsion polymerization; the effects of three types of surfactant, SDS (anionic), CTAB (cationic) and NPE (non-ionic), on the particle size of the resultant polymers were investigated in this work.

The TEM images of PMMA nanoparticles synthesized in SDS (anionic) micellar solution appeared as homogeneous spherical shapes [Figure 2(a)], and their diameter sizes varied from 13–18 nm. [Figure 2(b)] presents the TEM image of the PMMA nanoparticles polymerized with CTAB micelles, which appeared as spherical shapes 39–62 nm in diameter. In the NPE micellar solution, some precipitates, which had an irregular sphere like shapes and ranged from 6 to 13 nm in diameter, were observed, as shown in the TEM image in [Figure 2(c)]. In our study, we expected that NPE is the best in terms of reducing the particle size of PMMA because: (1) relatively high SDS concentration (>

cmc) might have increased the aggregation number and micellar size. (2) The cationic surfactants contain amine compounds which can be easily oxidized by the peroxide initiator.

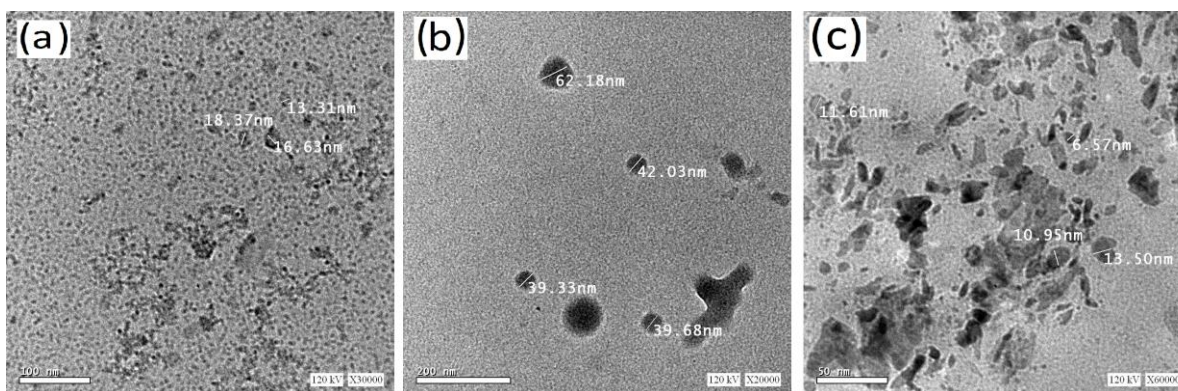


Figure 2 TEM of nanoparticle PMMA synthesized in (a) anionic, (b) cationic, and (c) nonionic micellar solutions

From [Figure 2], it can be seen that the polymer particles are very uniform and are nearly spherical. Combining the results of [Figure 2], very important information is obtained, namely that the nanosize PMMA particles can be obtained conveniently by the microemulsion polymerization. This result is very important and practical, and useful for industrialization of the microemulsion polymerization technique.

3. XRD

The XRD patterns of the PMMA nanoparticles synthesized with different types of surfactants (anionic, nonionic, and cationic) is presented in [Figure 3]. All the samples are taken in powder form.

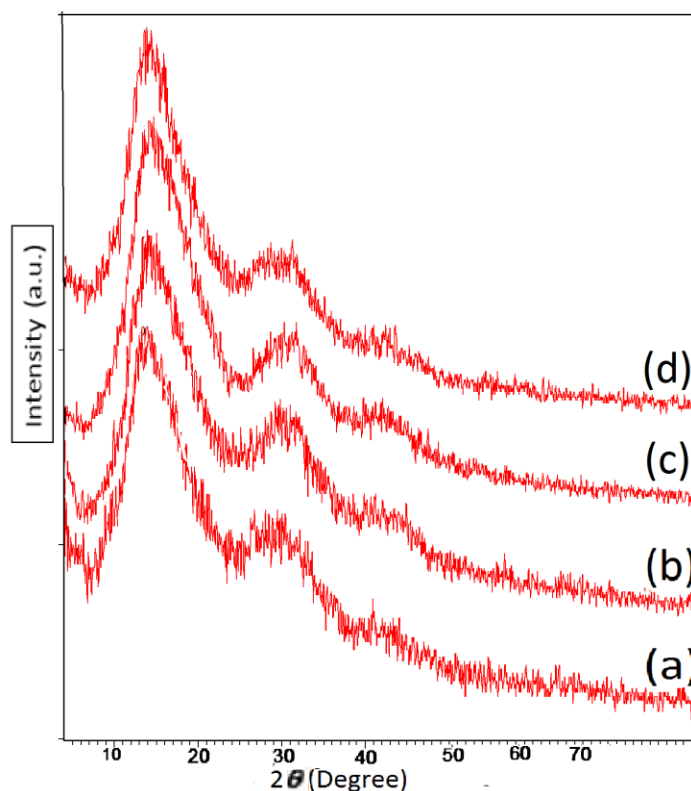


Figure 3 XRD patterns of PMMA synthesized in (a) anionic, (b) cationic, and (c) nonionic surfactants and (d) without surfactants

Pure PMMA shows a predominant and broad peak with a maximum at $2\theta = 15^\circ\text{C}$ along with broad but low-intensity peaks at 30°C and 41°C . These broad peaks indicate the amorphous nature of the polymer^[36].

All of the XRD peaks of PMMA are relatively broad, which confirms the small size of PMMA nanoparticles. The X-ray diffraction pattern indicates the amorphous nature with large diffraction maximum that decreases at large diffraction angles. The shape of the first main maximum indicates the ordered packing of the polymer chains. The intensity and shape of the second maxima are related to the effect inside the main chains^[37]. The observed broad humps in the XRD spectrum indicate the presence of crystallites of very low dimensions^[38].

The XRD patterns of the PMMA nanoparticles were similar to that of PMMA, as shown in [Figure 3(a-d)]. These results were consistent with the results of the FTIR analysis. For that, there was no difference between the PMMA and PMMA nanoparticles.

The diffraction peaks of PMMA have no change by adding surfactants. This indicates that the surfactants molecules do not enter into the nanoparticles, they only get absorbed on the surface of the particles.

4. Electrical Conductivity Measurements

The electrical conductivity σ ($\Omega^{-1}\text{cm}^{-2}$) was calculated from Equation (1)

$$\sigma = \frac{1}{\rho} \quad (1)$$

Where ρ (Ωcm^2) is the specific resistance of the materials and is calculated from Equation (2)

$$\rho = \frac{(R \times A)}{L} \quad (2)$$

Where R (Ω) is the resistance, A (cm^2) is the total area, and L (cm) is the thickness of the sample.

Table 1 Conductivity (S/cm) of the Synthesized PMMA Nanoparticles

Sample	Conductivity
PMMA –bulk	1.25×10^{-9}
PMMA–CTAB	2.13×10^{-9}
PMMA–SDS	2.19×10^{-9}
PMMA–NPE	2.60×10^{-9}

Table I shows that the conductivities of the PMMA nanoparticles prepared in SDS, CTAB, and NPE micelles were highest compared with those of the particles formed in bulk aqueous solution according to the following order: NPE > SDS > CTAB > Bulk aqueous solution. This may have been due to the fact that, the polymerization reaction in surfactant micellar solution occurred in the confined space of micelles, the density of the PMMA particles formed was higher than that of particles formed in bulk aqueous solution^[39]. PMMA nanoparticles can be applied as optically transparent conducting materials because of their high conductivity and ultrafine nanosize.

The obtained values were situated between the two extremes of those of semiconductors (10^{-10} – $10^{-2}\ \Omega^{-1}\text{cm}^{-1}$).^[40]

5. TGA

TGA measurement of nano-PMMA was performed under an N₂ atmosphere. The TGA curves for the PMMA synthesized in aqueous solution with and without the SDS, NPE, and CTAB micelle templates are compared in [Figure 4].

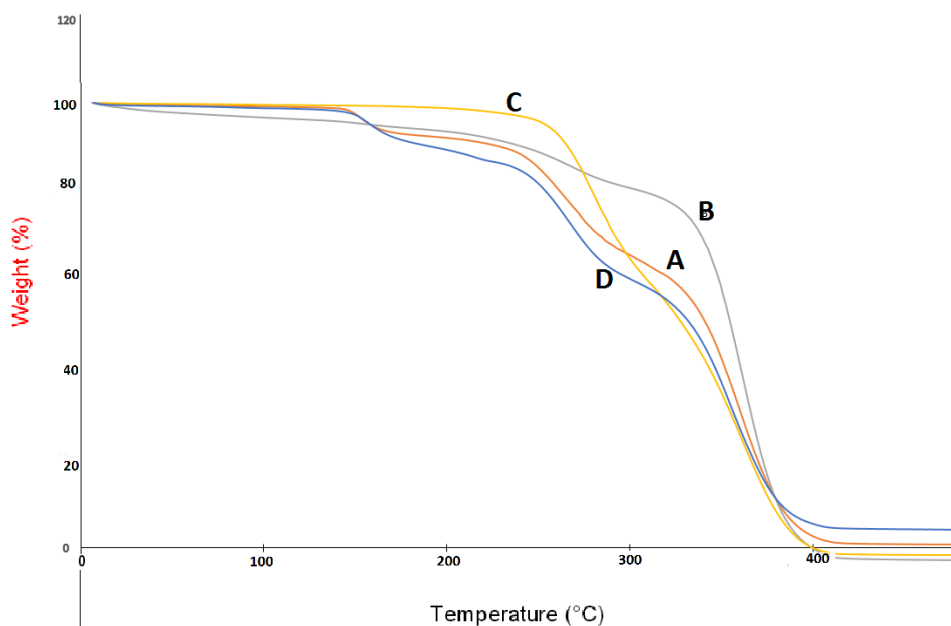


Figure 4 TGA of PMMA in (a) anionic, (b) cationic, and (c) nonionic surfactants and (d) without surfactants

Pure poly (methyl methacrylate) is deemed to have poor thermal behavior. A study of thermal degradation temperature of PMMA by TG exhibited that the polymer degrades in three steps at 180°C, 250°C and 350°C with a heating rate of 10 °C min⁻¹[41]. In our study, the weight loss observed in the temperature range from room temperature up to 100°C for all of the samples corresponded to water molecules/moisture, and the weight loss of PMMA [Fig. 3(a–d)] at temperatures up to 250°C was attributed to the loss of oligomers, and the weight loss beyond 250 up to 500°C was due to the degradation of the polymer main chain. As shown by TGA [Fig.4(a–d)], the rate of weight loss of PMMA was in the following order:

PMMA– SDS > PMMA– NPE > PMMA–CTAB > PMMA–bulk, respectively

Conclusion:

In this study, anionic (SDS), nonionic (NPE), and cationic (CTAB) micelles were used as polymerization media to produce PMMA nanoparticles. The use of surfactants as templates in the synthesis of conducting PMMA may offer new possibilities for the fabrication of PMMA with different morphologies, thermal stabilities. We found that the nanocomposites had a good thermal stability and higher electrical conductivity than the pristine polymer.

References

- [1] Bahaa Hussien (2011): The D.C and A.C Electrical Properties of (PMMA -Al₂O₃) Composites. *European Journal of Scientific Research*, 52(.2) , pp.236-242
- [2] Rao, J. P., & Geckeler, K. E. (2011). Polymer nanoparticles: preparation techniques and size-control parameters. *Progress in Polymer Science*, 36(7), 887-913.
- [3] Xu, H., Cheng, L., Wang, C., Ma, X., Li, Y., & Liu, Z. (2011). Polymer encapsulated upconversion nanoparticle/iron oxide nanocomposites for multimodal imaging and magnetic targeted drug delivery. *Biomaterials*, 32(35), 9364-9373.

- [4] Shang, S., Li, L., Yang, X., & Wei, Y. (2009). Polymethylmethacrylate-carbon nanotubes composites prepared by microemulsion polymerization for gas sensor. *Composites Science and Technology*, 69(7), 1156-1159.
- [5] Cannizzo, C., Amigoni-Gerbier, S., & Larpent, C. (2005). Boronic acid-functionalized nanoparticles: synthesis by microemulsion polymerization and application as a re-usable optical nanosensor for carbohydrates. *Polymer*, 46(4), 1269-1276.
- [6] G.R. Deen, L.H. Gan, Y.Y. Gan (2004):*Polymer*, 45 (16) , pp. 5483-5490
- [7] Ho, B. S., Tan, B. H., Tan, J. P., & Tam, K. C. (2008). Inverse microemulsion polymerization of sterically stabilized polyampholyte microgels. *Langmuir*, 24(15), 7698-7703.
- [8] S. Desbief, N. Hergue, O. Douheret, M. Surin, P. Dubois, Y. Geerts (2012): *Nanoscale*, 4 (8) , pp. 2705-2712
- [9] T.V. Magdesieva, O.M. Nikitin, O.A. Levitsky, V.A. Zinovyeva, I. Bezverkhyy, E.V. Zolotukhina, (2012): *Journal of Molecular Catalysis A: Chemical*, 353 , pp. 50-57
- [10] Huang, H., Liu, Y., Lee, S. T., & Kang, Z. (2012). Polymer (polyaniines) nanoparticles: a superior catalyst for hydrocarbon selective oxidation. *Journal of Materials Chemistry*, 22(2), 337-340.
- [11] Pinheiro, J. P., Moura, L., Fokkink, R., & Farinha, J. P. S. (2012). Preparation and characterization of low dispersity anionic multiresponsive core-shell polymer nanoparticles. *Langmuir*, 28(13), 5802-5809.
- [12] M. Chen, C. Zhou, Z.G. Liu, C.L. Cao, Z. Liu, H.D. Yang (2010): *Polymer International*, 59 (7) , pp. 980-985
- [13] Unsworth, J., Lunn, B. A., Innis, P. C., Jin, Z., Kaynak, A., & Booth, N. G. (1992). Technical review: conducting polymer electronics. *Journal of intelligent material systems and structures*, 3(3), 380-395.
- [14] Angelopoulos, M. (2001). Conducting polymers in microelectronics. *IBM Journal of Research and Development*, 45(1), 57-75
- [15] Meng, X., Zhang, Z., Luo, N., Cao, S., & Yang, M. (2011). Transparent poly (methyl methacrylate)/TiO₂ nanocomposites for UV-shielding applications. *Polymer Science Series A*, 53(10), 977-983.
- [16] Sivakkumar, S. R., Kim, W. J., Choi, J., MacFarlane, D. R., Forsyth, M., & Kim, D. W. (2007). Electrochemical performance of polyaniline nanofibres and polyaniline/multi-walled carbon nanotube composite as an electrode material for aqueous redox supercapacitors. *Journal of power sources*, 171(2), 1062-1068.
- [17] Erokhin, V., Berzina, T., & Fontana, M. P. (2005). Hybrid electronic device based on polyaniline-polyethyleneoxide junction. *Journal of applied physics*, 97(6), 064501.
- [18] Chiou, N. R., & Epstein, A. J. (2005). Polyaniline nanofibers prepared by dilute polymerization. *Advanced Materials*, 17(13), 1679-1683.
- [19] Meng, X., Zhang, Z., Luo, N., Cao, S., & Yang, M. (2011). Transparent poly (methyl methacrylate)/TiO₂ nanocomposites for UV-shielding applications. *Polymer Science Series A*, 53(10), 977-983.
- [20] Sivakkumar, S. R., Kim, W. J., Choi, J., MacFarlane, D. R., Forsyth, M., & Kim, D. W. (2007). Electrochemical performance of polyaniline nanofibres and polyaniline/multi-walled carbon nanotube composite as an electrode material for aqueous redox supercapacitors. *Journal of power sources*, 171(2), 1062-1068.
- [21] Erokhin, V., Berzina, T., & Fontana, M. P. (2005). Hybrid electronic device based on polyaniline-polyethyleneoxide junction. *Journal of applied physics*, 97(6), 064501.
- [22] Chiou, N. R., & Epstein, A. J. (2005). Polyaniline nanofibers prepared by dilute polymerization. *Advanced Materials*, 17(13), 1679-1683.
- [23] Norakankorn, C., Pan, Q., Rempel, G. L., & Kiatkamjornwong, S. (2007). Synthesis of Poly (methyl methacrylate) Nanoparticles Initiated by 2, 2' - Azoisobutyronitrile via Differential Microemulsion Polymerization. *Macromolecular rapid communications*, 28(9), 1029-1033.
- [24] Stevens, Malcolm P. (1998): *Polymer Chemistry: An Introduction*. Oxford University Press, USA.
- [25] Van Krevelen, D.W.(2003):*Properties of polymers*, ELSEVIER.
- [26] Harper, Charles A.(2005): *Handbook of Plastic Processes*, John Wiley & Sons.
- [27] Harper, Charles A., Edward M. Petrie. (2003)*Plastics Materials and Processes* John Wiley & Sons.
- [28] Crawford, R. J. (1998): *Plastics engineering*. Butterworth Heinemann.
- [29] Järvelä P.(2000): *Ruiskuvalu, Plastdata*
- [30] Sivakkumar, S. R.; Kima, W. J.; Chou, J. A.; MacFariane, D.R.; Forsyth, M.; Kima, D. W. *J Power Sources* 2007, 171,1062.
- [31] Erokhin, V.; Berzina, T.; Fontana, M. P. *J Applied Physics* 2005, 97,064501.

- [32] Ramya, G.; Renugadevi, C.; Rao, C. R. K.; Trivedi, D. C. *Reactive and Functional Polymers* 2008, 68, 701.
- [33] Chiou, N. R.; Epstein, A. J. *Advanced Material* 2005, 17, 1679.
- [34] Steijskal, J.; Sapurina, I.; Trchova, M.; Konyushenko, E. N.; Holler, P. *Polymer* 2006, 47, 8253.
- [35] Fendler, J. H. *Membrane Mimetic Chemistry: Characterizations and Applications of Micelles, Microemulsions, Monolayers, Bilayers, Vesicles, Host-Guest Systems, and Polyions*; Wiley: New York, 1982; pp 6, 206.
- [36] P. Kamaraj, M. Arthanareeswari, S. Devikala. *Chemical Science Transactions*, 2013, 2(S1), S129-S134.
- [37] Chandar Shekar B, Na M, Lee J & Rhee S W, *Molecular Crystals and Liquid Crystals*, 424 (2004) 43.
- [38] S Sathish & B Chandar Shekar *Indian Journal of Pure & Applied Physics* 52 (2014), PP.64-67
- [39] Pillai, V.; Kumar, P.; Hou, M. J.; Ayyub, P.; Shah, D. O. *Advanced Colloid Interface Science* 1995, 55, 241.
- [40] Goodings, E. P. 1976. *Chem. Soc. Rev.*, 5: 95-119 [CrossRef], [Web of Science ®]
- [41] C. Dong, X. Ni, J. *Macromol. Sci. A*.41, 547 (2004).

© 2016, by the Authors. The articles published from this journal are distributed to the public under “**Creative Commons Attribution License**” (<http://creativecommons.org/licenses/by/3.0/>). Therefore, upon proper citation of the original work, all the articles can be used without any restriction or can be distributed in any medium in any form.

Publication History

Received 26th Jan 2016
Revised 12th Feb 2016
Accepted 24th Feb 2016
Online 30th Mar 2016