

Co(III) Complex Mediated Microwave-Assisted Synthesis of PAN

Trinath Biswal, Ramakanta Samal, Prafulla K. Sahoo

Department of Chemistry, Utkal University, Vani Vihar, Bhubaneswar 751004, India

Received 29 September 2009; accepted 22 January 2010

DOI 10.1002/app.32166

Published online 29 March 2010 in Wiley InterScience (www.interscience.wiley.com).

ABSTRACT: Free radical polymerization of acrylonitrile (AN) is efficiently, easily, and quickly achieved in the presence of Co(III) complex, $[\text{Co(III)}(\text{en})_3]\text{Cl}_3$ and ammonium persulphate (APS) in domestic microwave oven. The rate of polymerization depends on the power and time of microwave irradiation, and is independent of the technique employed (periodic or continuous irradiation). The conversion of monomer to the polymer was mostly excellent in gram scale. Irradiation at low power and time produced more homogeneous polymers with high molecular weight and low polydispersity when compared with the polymer formed by conventional heating method. The interaction of reacting components was monitored by UV-visible spectrometer. The average molecular weight was

derived by GPC and viscosity methods and sound velocity by ultrasonic interferometer. The uniform and reduced molecular size was characterized by transmission electron microscopy, the diameter of PAN particles being in the range 220–250 nm in microwave and 120–530 nm in conventional heating methods. From the kinetic results, the rate of polymerization (R_p) was expressed as

$$R_p = K[\text{Co(III)}]^{0.33}[\text{APS}]^{0.31}[\text{AN}]^{0.88}$$

© 2010 Wiley Periodicals, Inc. *J Appl Polym Sci* 117: 1837–1842, 2010

Key words: microwave; complex catalyst; kinetics

INTRODUCTION

Recently, there has been growing interest in applying microwave energy to synthetic organic chemistry.^{1–5} Microwave heating has also been used as the activation method for a number of polymerization reactions. The main advantages of microwaves over traditional heating (hot plates, bunsen burner, etc.) for preferring an organic reaction are an increased rate of production, shorter reaction time (usually 1/1000), improved product characteristics, uniform processing, less floor space required, and convenience and controllability of the process.^{6–10} The mechanism of energy transfer using microwave field is considerably different from the well-established modes (radiation, conduction, and convection) of heat transfer. Thus, microwave heating is the first new heating technique in the millions of year since the discovery of fire. This kind of heating is based on the ability of some liquids and solids to transform electromagnetic energy into heat^{11–13} and it has revolutionized cooking and chemistry.

Since 1986, the number of organic reactions assisted by this new kind of heating has increased enormously.¹⁴ The microwave irradiation can be used for the preparation of nanocomposites¹⁵ via *in situ* polymerization,¹⁶ nonconducting and cross-linked polymers,¹⁷ graft copolymers,^{18,19} and optical polymers.²⁰ Although different kinds of microwave reactors are described in the literature,^{21,22} recently it is demonstrated the diverse organic reactions can be safely performed in a conventional domestic microwave oven.²³ These advantages turn the microwave-assisted approach environmentally benign for the preparation of important compounds and the technology very attractive to industry for its smaller and uniform particle (polymer molecule) size.

In our previous publications we have synthesized PAN using Cu(II)/H₂ Salen/KHSO₅/AN/H₂O,²⁴ Cu(II)/glycine/KHSO₅/AN/H₂O,²⁵ Cu(II)/EDTA/APS/MMA^{26,27} via emulsifier free emulsion process in conventional heating methods, studied their kinetics and other properties. However, in this article, we have prepared PAN using $[\text{Co(III)}(\text{en})_3]\text{Cl}_3$ /APS in domestic microwave oven and studied its kinetics and other properties like molecular weight, particle size. Acrylonitrile (AN) is a challenging monomer because of its high reactivity and the poor solubility of PAN. PAN and its copolymer are used in several potential applications, such as the preparation of carbon fibers, nanometer carbon tubes,

Correspondence to: P. K. Sahoo (psahoochemuu@satyam.net.in).

membrane materials, etc. Further studies regarding the preparation of copolymers and composites are currently underway.

EXPERIMENTAL

Materials

Monomer AN from Emerck India, was purified as reported earlier.²⁸ The initiator APS and all other reagents like Cobalt (III) Chloride, ethylene diamine (en), etc. were purchased from Emerck India (AR grade) and used after purification by standard techniques.

Preparation of [Co(III)(en)₃]Cl₃ complex

It was prepared by the method available in literature.²⁹ 61 g of 30% ethylene diamine was partly neutralized with 17 mL of 6N hydrochloric acid and the resulting mixture was poured into a solution of 24 gm of cobalt (II) chloride 6-hydrate in 75 mL of water. The cobalt was oxidized by bubbling a vigorous stream of air through the solution for 3 h. The solution was allowed to evaporate on a steam bath until a crust began to form over the surface (the volume was about 15 to 20 mL); then 15 mL concentrated hydrochloric acid and 30 mL ethyl alcohol were added. After cooling, the crystals of tris(ethylene diamine)cobalt(III) chloride were filtered and washed with alcohol until the washings were colorless. They were then washed with ether and dried in an oven.

Synthesis of PAN

Microwave oven

The polymerization experiments were carried out in a Kenstar (Model No. MOW 9811, 1200 W) domestic microwave oven. The average bulk temperature at end of the reaction was measured by inserting a thermometer in the reaction mixture. All the experiments were done with water as solvent and the temperatures less than 100°C. For all the MW powers studies, the exposure time was varied from 30 s to 360 s. The reactions were carried with requisite amount of [Co(III)(en)₃]Cl₃, AN, and APS in N₂ atmosphere.

Conventional heating

The polymerization were carried out in a reaction vessel containing known concentrations of [Co(III)(en)₃]Cl₃ and the monomer AN in N₂ atmosphere. The solutions were stirred at 400–500 rpm, which helped in the formation of micelles in the complex medium. After maintaining constant temperature

50°C, the requisite amount of initiator solution was carefully injected to the reaction mixture.

After the desired time both in microwave oven and conventional heating, the polymerization was terminated by keeping the reaction vessel in ice-cold water and by adding a known excess of hydroquinone, which spontaneously consumed the unreacted free radicals.²⁶ The precipitated polymers were filtered and purified by washing repeatedly with distilled water and absolute alcohol. Then they were dried till a constant weight at 40°C. The percentage conversion and the rate of polymerization (R_p) were determined gravimetrically.

Characterization

The UV-visible spectra of [Co(III)(en)₃]Cl₃ complex *vis-à-vis* those of the monomer and the initiator were studied using a Perkin-Elmer UV-visible spectrophotometer model Lambda-20.

The average molecular weights of the purified samples were determined by widely used methods, such as GPC (\overline{M}_n) and intrinsic viscosity (\overline{M}_v) using the relationship of Mark-Houwink-Sakurada³⁰ in pure benzene at 30°C: $[\eta] = 5.20 \times 10^{-5} \overline{M}_v^{0.7}$.

Sound velocity of the sample solution was measured with an ultrasonic interferometer, Mittal enterprises, New Delhi, India.

Uniform structure of PAN was investigated by means of TEM (H-7100 Hitachi Co), operated at an accelerating voltage of 100 kV.

RESULTS AND DISCUSSION

The results of the study on the polymerization of AN initiated by APS catalyzed by [Co(III)(en)₃]Cl₃ are tabulated in Table I. From the results, it is evident that [Co(III)(en)₃]Cl₃ gave the maximum R_p and the order of R_p for various systems is as follows:

$$R_p(\text{APS} + [\text{Co(III)(en)}_3]\text{Cl}_3) > R_p(\text{APS})$$

UV-visible

The UV-visible spectra of various mixtures like [Co(III)(en)₃]Cl₃, [Co(III)(en)₃]Cl₃/APS, [Co(III)(en)₃]Cl₃/AN/APS before reaction and after reaction (by microwave oven and conventional method) were measured in an aqueous solution to obtain a complete picture of the interaction between the reacting species and their relationship with the rate data (Fig. 1). The bidentate ligand character of en with colored cations like Co(III) to form chelate complex is well recognized,³¹ where the Co(III) and en ratio in complex Scheme 1(a) is 1 : 3 as evidenced by the proportionality found in the rate expression. Further, the central metal ion, Co(III) is coordinated to three

TABLE I
Effect of Concentration of AN, APS, and $[\text{Co(III)en}_3]\text{Cl}_3$ on the % Conversion and R_p by Microwave and Conventional Processes and \overline{M}_v , \overline{M}_n by Viscosity and GPC Methods of PAN

$[\text{AN}] \times 10^{-2}$ (mol dm ⁻³)	$[\text{APS}] \times 10^{-3}$ (mol dm ⁻³)	$[[\text{Co(III)en}_3]\text{Cl}_3]$ $\times 10^{-3}$ (mol dm ⁻³)	Microwave Irradiation Process		Conventional Heating Process		Molecular Weight by Microwave Process	
			Conversion (%)	$R_p \times 10^6$ mol (dm ⁻³ s ⁻¹)	Conversion (%)	$R_p \times 10^8$ (mol dm ⁻³ s ⁻¹)	$\overline{M}_v \times 10^{-6}$ Viscosity	$\overline{M}_n \times 10^{-6}$ GPC
0.0	10.0	10.0	0.0	0.0	0.0	0.0	–	–
0.5	10.0	10.0	84.45	2.35	56.45	4.4	0.9	0.68
1.0	10.0	10.0	85.85	4.24	57.12	8.28	1.09	0.81
1.5	10.0	10.0	86.04	6.02	57.95	11.8	1.24	1.07
2.0	10.0	10.0	86.54	7.69	58.56	15.39	1.64	1.32
2.5	10.0	10.0	86.48	9.15	65.98	20.1	1.86	1.51
3.0	10.0	10.0	85.56	10.87	64.56	21.24	2.09	1.69
3.5	10.0	10.0	84.48	11.94	62.65	23.54	2.24	1.8
2.0	0.0	10.0	0.0	0.0	0.0	0.0	–	–
2.0	2.5	10.0	54.54	4.02	32.45	10.48	–	–
2.0	5.0	10.0	71.56	5.79	45.56	13.72	–	–
2.0	10.0	10.0	86.54	7.69	58.56	15.39	–	–
2.0	15.0	10.0	86.78	8.12	60.32	17.36	–	–
2.0	20.0	10.0	86.96	8.31	62.50	17.9	–	–
2.0	25.0	10.0	87.08	8.6	63.48	18.14	–	–
2.0	10.0	0.0	10.2	1.2	1.7	0.12	–	–
2.0	10.0	2.5	67.42	4.99	44.98	12.05	–	–
2.0	10.0	5.0	75.54	5.71	49.36	13.56	–	–
2.0	10.0	10.0	86.68	7.69	58.56	15.39	–	–
2.0	10.0	15.0	87.69	8.64	59.02	16.64	–	–
2.0	10.0	20.0	88.12	9.32	60.0	17.52	–	–
2.0	10.0	25.0	89.23	9.98	60.45	18.25	–	–

The polymerization rate (R_p) in microwave oven for 240 s and in conventional heating at 50°C for 3 h.

molecules of monomer (AN), (Complex-II, Scheme 1(b) as revealed from the sharp change in absorbance from 1.2(a) to 1.48(b) in Figure 1 which is also accorded from the rate expression. On addition of the initiator (APS), to the above mixture (Complex-II), the absorbance reduces from 1.48(b) to 1.3(c) showing the initiation of polymerization, thus establishing the mechanism of complex initiation as evidenced by change in absorbance from 1.3(c) to 0.67(d) after polymerization. The high conversion values with $[\text{Co(III)(en)}_3]\text{Cl}_3$ complex may be due to the high rate production of initiating radicals generated by the heterolysis of the initiator bound by a complex of $[\text{Co(III)(en)}_3]\text{Cl}_3$ where the internal energy is transferred to the monomer. The new non-conventional complex initiated system leads to stabilizing the emulsion latex to a high conversion in absence of an added emulsifier.

It was found that the conversion and the R_p were strongly affected by the monomer, initiator and complex concentrations and also by the reaction time. The detailed kinetics is discussed as follows:

Variation of time

Figure 2 shows the variation and comparison of conversion with reaction time under microwave and

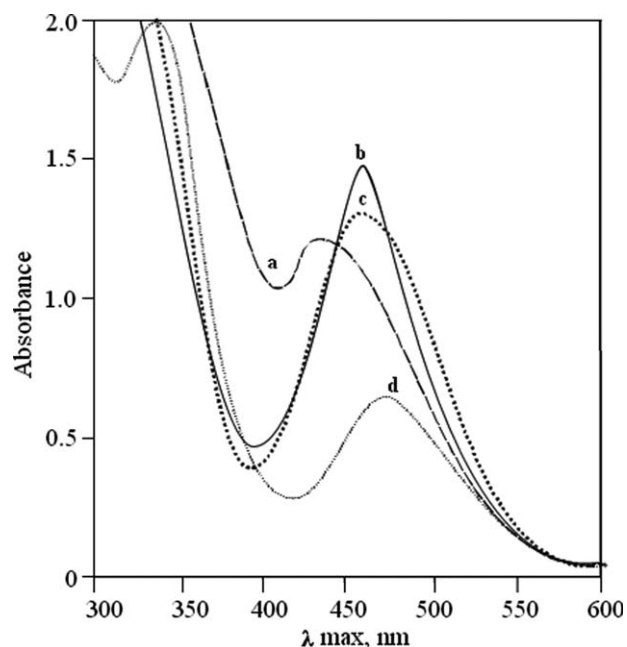
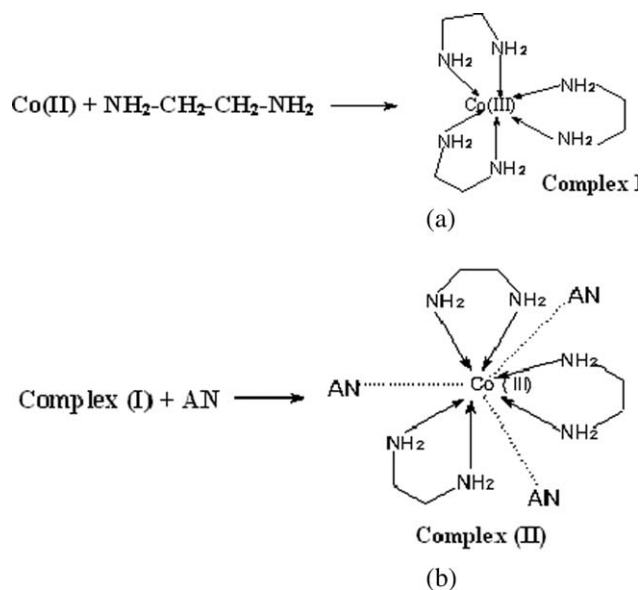


Figure 1 UV-visible spectral evidence for the formation of $[\text{Co(III)en}_3]\text{Cl}_3$ and interaction with APS taking AN as monomer. $[\text{Complex}] = 10.0 \times 10^{-3}$ mol dm⁻³, $[\text{AN}] = 2.0 \times 10^{-2}$ mol dm⁻³, $[\text{APS}] = 10.0 \times 10^{-3}$ mol dm⁻³ (a) $[\text{Co(III)en}_3]\text{Cl}_3$, (b) $[\text{Co(III)en}_3]\text{Cl}_3 + \text{AN}$, (c) $[\text{Co(III)en}_3]\text{Cl}_3 + \text{AN} + \text{APS}$ before reaction, and (d) $[\text{Co(III)en}_3]\text{Cl}_3 + \text{AN} + \text{APS}$ after reaction by microwave oven.



Scheme 1 (a) Formation of $[\text{Co(III)(en)}_3]\text{Cl}_3$ complex, (b) coordination of monomer AN with $[\text{Co(III)(en)}_3]\text{Cl}_3$

traditional heating process keeping the concentrations of AN, APS and $[\text{Co(III)(en)}_3]\text{Cl}_3$ constant at 2×10^{-3} and 10×10^{-3} mol dm⁻³, respectively. It was found that the polymerization reaction is very fast in microwave oven and showed a dead end polymerization tendency, i.e., the initiation activity of the initiator is high at initial period and hence after 240 s it increases at a comparatively slow rate. But in case of traditional heating more time was required, i.e., 3 h for production as compared to microwave irradiation.

Variation of monomer concentration

The conversion and the rate of polymerization reaction increase with the increase in monomer concentration ($0.5\text{--}3.5$ mol dm⁻³) at fixed concentration of the other reagents and components. The results are tabulated in Table I. From the double logarithmic plot of R_p vs. $[\text{AN}]$, the rate of polymerization was found to be 0.88 powers dependent on the monomer concentration. This order may be attributed to the greater rate of participation of the monomer in the initiation step. Less than one value of order has also been cited in the literature as Chapiro³² found the monomer exponent varying from one to less than one, and the findings were attributed to the presence of impurity in the polymerization system. In addition, the deviation from unity or more than unity is normally observed as the polymerization system becomes heterogeneous in nature.³³

The molecular weights \overline{M}_v and \overline{M}_n of the polymer, as determined by viscosity and GPC methods, increase from 0.9×10^6 to 2.4×10^6 and 0.68×10^6

to 1.8×10^6 , respectively with increasing $[\text{AN}]$ from 0.5 to 3.5×10^2 mol dm⁻³.

Variation of initiator concentration

The effects of the R_p and the conversion have been studied by varying the concentration of the initiator in the range 2.5×10^{-3} to 25.0×10^{-3} mol dm⁻³ as given in Table I. With the increase in APS concentration in the above range the conversion and R_p were found to increase because of an increase in concentration of the active species resulting in smaller oligomers with higher critical micelle concentration. The double logarithmic plot gave a regular increasing trend with the order of 0.31.

Variation of $[\text{Co(III)(en)}_3]\text{Cl}_3$ concentration

From Table I, it was found that the R_p and % conversion of AN were negligible in absence of $[\text{Co(III)(en)}_3]\text{Cl}_3$ complex both in conventional heating and in microwave irradiation processes. However, the R_p and % conversion with increase in $[\text{Co(III)(en)}_3]\text{Cl}_3$ concentration were found to increase uniformly (Table I). The impact of $[\text{Co(III)(en)}_3]\text{Cl}_3$ on R_p was found from the double logarithmic plot, the order of the reaction with respect to the $[\text{Co(III)(en)}_3]\text{Cl}_3$ concentration was observed to be 0.33. The effect of the complex on R_p was also described earlier.

Chain transfer

Figure 3 shows the relationship between R_p and the reciprocal of degree of polymerization ($1/\text{DP}$) of PAN observed when the $[\text{APS}]$ was varied at a fixed $[\text{AN}]$.

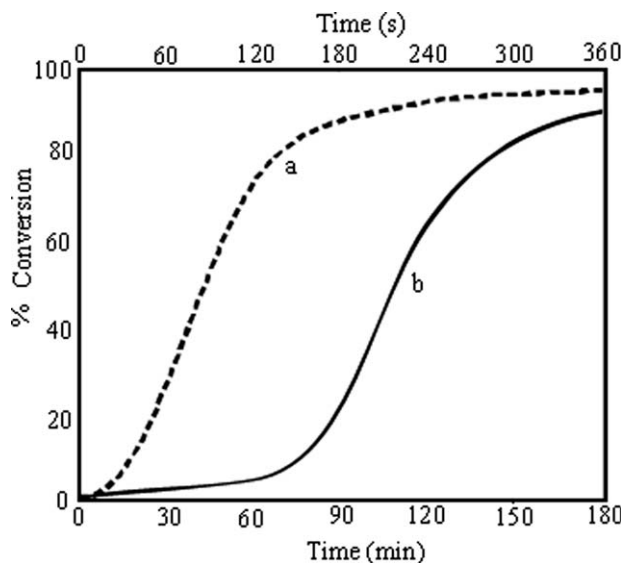


Figure 2 % conversion PAN (a) in microwave oven and (b) in conventional heating.

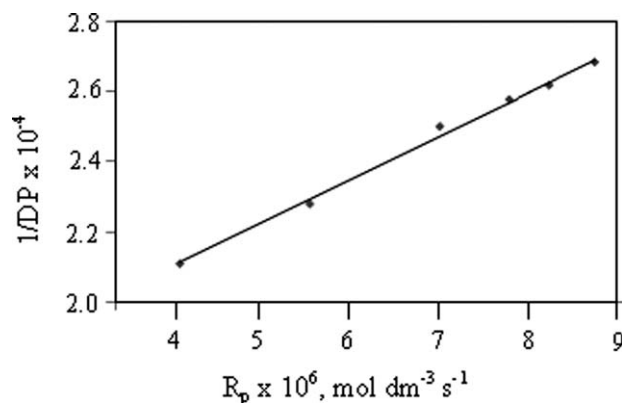


Figure 3 Dependence of the reciprocal of degree of polymerization ($1/DP$) of AN on R_p on varying $[APS]$ from 2.5×10^{-3} to $25 \times 10^{-3} \text{ mol dm}^{-3}$ at $[AN] = 2 \text{ mol dm}^{-3}$ and $[Co(III)en_3Cl_3] = 10 \times 10^{-3} \text{ mol dm}^{-3}$.

A linear relationship observed here excludes any significant chain transfer to the initiator in the polymerization of AN with APS and $[Co(III)(en)_3]Cl_3$.

Ultrasonic velocity

Ultrasonic velocity data reveal that the sound velocity increases with the increase in molecular weight (Fig. 4). The data are in similar trend noticed in case of poly(ethylene glycol) as reported by Gerecse.³⁴ From Figure 4, it is found that the sound velocity is smoothly increases with increasing molecular weight of PAN without any more deviation, i.e., the value is nearly uniform because of the uniform particle size.

Particle morphology by TEM

From TEM Figure 5, it was found that the particle formed by microwave irradiation is more uniform and smaller [Fig. 5(a)] than the particle formed in thermal irradiation [Fig. 5(b)]. The results are similar with those of the report by Bao et al.³⁵ The variations of particle size with complex concentration are tabulated in Table II for both processes.

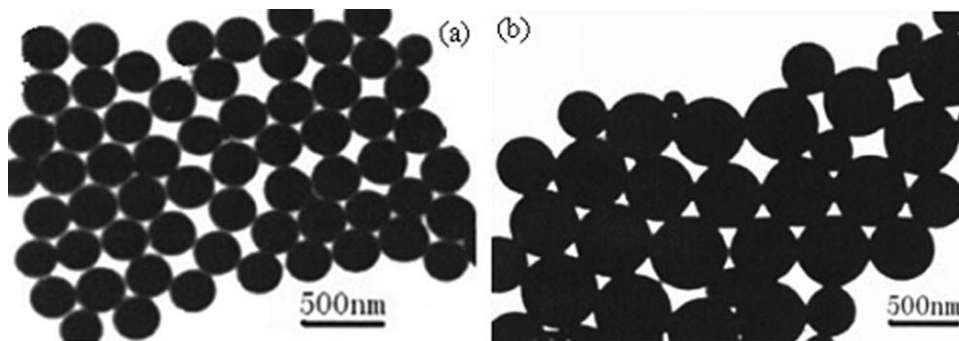


Figure 5 Particle size of PAN, prepared by (a) microwave irradiation and (b) thermal irradiation.

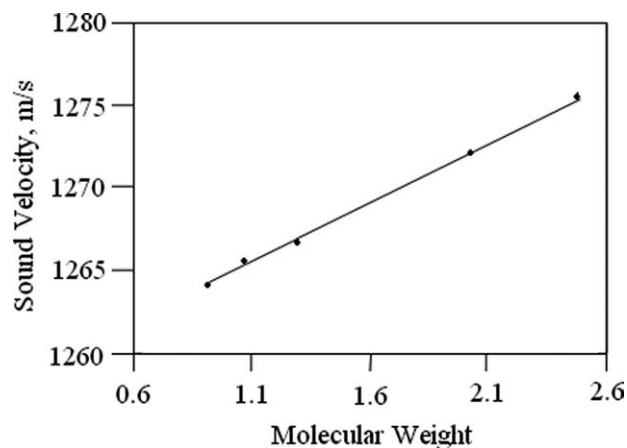


Figure 4 Variation of sound velocity with molecular weight of PAN solution in DMF at 30°C .

Mechanism

The mode of initiator decomposition, chain initiation, and termination mechanism of polymerization involving the novel catalytic system $[Co(III)(en)_3]Cl_3/APS$ can be interpreted as follows:

Chain initiation by $Co(III)(en)_3Cl_3/APS$ complex



The above complexation mechanism is explained earlier on the spectral data and Scheme 1(a,b)

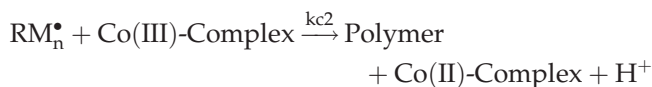
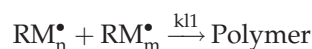
Propagation



TABLE II
Variation of Particle Size in Microwave and
Conventional Processes at Different Concentrations of
Complex at [AN] = 2.0 mol dm⁻³,
[APS] = 10.0 mol dm⁻³

[[Co(III)en ₃]Cl ₃] mol dm ⁻³	Diameter of particle in nm	
	Microwave process	Conventional process
2.5	220	120
5.0	227	301
10.0	235	364
15.0	242	427
20.0	247	483
25.0	250	530

Termination



Applying steady state principle and assuming mutual termination, the rate of expression is observed as follows:

$$R_p \propto [\text{Co(III)}]^{0.33} [\text{APS}]^{0.31} [\text{AN}]^{0.88}$$

CONCLUSIONS

PAN was prepared by cost effective, nonconventional emulsifier-free emulsion technique using domestic microwave oven. In microwave oven, the polymerization took place very fast and consumed very less time, the molecular weight is high and also the particle size is more uniform and small, which was conformed using TEM. The fast polymerization reactions were carried by fast decomposition of initiator because of the complex initiation. The polymerization process was further characterized by UV-visible spectra, ultrasonic velocity, and molecular weight measurements. Hence, it is a promising technique for the preparation of polymer.

References

- Goretziki, C.; Krlej, A.; Steffens, C.; Ritter, H. *Macromol Rapid Comm* 2004, 25, 513.
- Iannelli, M.; Alupei, V.; Ritter, H. *Tetrahedron* 2005, 61, 1509.
- Iannelli, M.; Ritter, H. *Macromol Chem Phys* 2005, 206, 349.
- Bezduzhna, E.; Ritter, H. *Macromol Rapid Comm* 2007, 28, 443.
- Buolamwini, J. K. *J Med Chem* 2006, 49, 7922.
- Zhu, X.; Zhou, N.; He, X.; Cheng, Z.; Lu, J. *J Appl Polym Sci* 2003, 88, 1787.
- Hayes, B. L. *Microwave Synthesis-Chemistry at the Speed of Light*; CEM Publishing: USA, 2002.
- Loupy, A., Ed. *Microwaves in Organic Synthesis*; Wiley-VCH: Germany, 2003.
- Nothdurft, L.; Bode, R.; Schmidt-Naake, G. *Macromol Symp* 2009, 275, 173.
- Mallakpour, S.; Mohammad, D. *Polym Adv Technol* 2008, 19, 1334.
- Zlotorzynski, A. *Crit Rev Anal Chem* 1995, 25, 43.
- Lee, S. H.; Lee, W. G.; Chung, B. G.; Park, J. H.; Khademhosseini, A. *Macromol Rapid Comm* 2009, 30, 1382.
- Sen, G.; Singh, R. P.; Pal, S. *J Appl Polym Sci* 2010, 115, 63.
- Caddick, S. *Tetrahedron* 1995, 51, 10403.
- Liu, S. J.; Huang, C. H.; Huang, C. K.; Hwang, W. S. *Electrochem Comm* 2009, 11, 1792.
- Cao, H.; Wang, P.; Weibo Yuan, W.; Lei, H. *J Appl Polym Sci* 2010, 115, 1468.
- Çelik, B. G.; Ksakurek, D. *J Appl Polym Sci* 2006, 102, 5427.
- Singh, V.; Tiwari, A.; Pandey, S.; Singh, S. K. *Starch-Starke* 2006, 58, 536.
- Morteza, N.; Mohammad, J. Z. M.; Ali, A. Y.; Amir, E. L. *Starch-Starke* 2009, 61, 188.
- Mallakpour, S.; Taghavi, M. *Eur Polym J* 2008, 44, 87.
- Strauss, C. R.; Trainor, R. W. *Aust J Chem* 1995, 48, 1665.
- Wiesbrock, F.; Hoogenboom, R. *Macromol Rapid Comm* 2004, 25, 1793.
- Bose, A. K.; Banik, B. K.; Lavlinskaia, N.; Jayaraman, M.; Manhas, M. S. *Chem-Tech* 1999, 1, 43.
- Sahoo, P. K.; Sahu, G. C.; Swain, S. K. *Euro Polym J* 2002, 38, 345.
- Sahoo, P. K.; Dey, M.; Swain, S. K. *J Appl Polym Sci* 1999, 74, 2785.
- Sahoo, P. K.; Mohapatra, R. *Euro Polym J* 2003, 39, 1839.
- Sahoo, P. K.; Samal, R. *Polym Degrad Stab* 2007, 92, 1700.
- Sahoo, P. K.; Bhattacharya, S. P.; Samal, R. K. *Euro Polym J* 1985, 21, 499.
- Fernelius, W. C., Ed. *Inorganic Syntheses*; Mc-Graw Hill: New York, 1946; Vol II, p 221.
- Kurata, M.; Tsunashima, Y. In *Polymer Handbook*, 4th ed.; Brandrup, J., Immergut, E. H., Eds. Wiley: New York, 1999; Vol. VII/1.
- Vogel, A. I. *Vogels textbook of quantitative inorganic analysis*; 4th ed.; ELBS and Longman: 1978; p 262.
- Chapiro, A. *J Chem Phys* 1995, 52, 568.
- Odian, G. *Principles of Polymerization*; 3rd ed.; Wiley: New York, 1981; p 205.
- Gerecze, N. G. *Acoustica* 1977, 38, 51.
- Bao, J.; Zhang, A. *J Appl Polym Sci* 2004, 93, 2815.