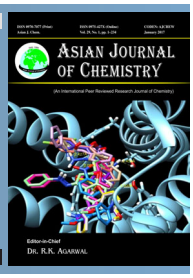
Asian Journal of Chemistry; Vol. 29, No. 2 (2017), 457-460

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2017.20283



Synthesis, Characterization and Radical Polymerization of Novel Furan Substituted Acrylamide

MUSTAFA TOMBUL*, ADNAN BULUT and HALIL ÜNVER

Department of Chemistry, Faculty of Science & Letters, Kirikkale University, 71450 Yahsihan, Kirikkale, Turkey

*Corresponding author: Fax: +90 318 3572461; Tel: +90 318 3574242/4037; E-mail: mtombul@kku.edu.tr

Received: 2 September 2016; *Accepted*: 7 November 2016; *Published online*: 30 November 2016; AJC-18180

N-[(Furan-2-yl)methyl]acrylamide (FMA) was synthesized *via* the reaction of furfurylamine with acryloyl chloride and the chemical structure was elucidated by ^{1}H NMR, ^{13}C NMR and FTIR analyses. Free radical polymerization of *N*-[(furan-2-yl)methyl]acrylamide was performed employing benzoyl peroxide (BPO) initiator under inert atmosphere of nitrogen in toluene. The monomer concentration and initiator concentration ranges were 8.8×10^{-2} to 13.2×10^{-2} mol L^{-1} and 3.4×10^{-3} to 20.7×10^{-3} mol L^{-1}, respectively. The rate of polymerization (R_p) was found to be $R_p = k[BPO]^{0.51}[FMA]^{1.69}$. The overall activation energy of 84 kJ mol^{-1} was obtained in the temperature range 70-90 °C. The FTIR spectra of the prepared polymer indicate disappearance of the band at 1620 cm^{-1}, which is basically due to the olefinic C=C stretching, confirming the polymerization of *N*-[(furan-2-yl)methyl]acrylamide.

Keywords: Radical polymerization, Furan, Arylamide.

INTRODUCTION

N-[(Furan-2-yl)methyl]acrylamide (FMA) is a prominent monomer containing both reactive amide and furfuryl group as the reactive diene functionality in the pendent group. In particular, thermoreversible and mendable materials can achievable through the Diels-Alder reaction utilizing a suitable dienophile with monomers consisting furan group [1-3]. Apart from the aforementioned peculiarities, these materials find usage area widely in biomedical applications [4-6].

Polymers having specific functionalities can be obtained by synthesizing novel monomers bearing the functional groups and thus desired objectives can be fulfilled [7-11]. The synthesis of polymers possessing well-defined compositions, functionalities and architectures has become a substantial topic in terms of polymer science. To that end, the use of acrylamide polymers and derivatives has rapidly increased especially during the last two decades. Poly(acrylamide) and derivatives have a good deal of applications such as adsorbent in the removal of heavy metal ion/dye from wastewater [12,13], as polymeric mediator for electrochemical biosensors [14], as fluid loss agent for oil well cement [15], as gene delivery vector [16] and as drug-delivery agent [17,18].

The preparation methods for novel functional acrylamide derivatives by the reaction between acryloyl chloride and corresponding amides has been reported [8,19-22]. This study deals mainly with the preparation of a novel acrylamide derivatives comprising a furan moiety. In this article, synthesis and characterization of the new monomer and its free radical polymerization will be discussed in detail. Moreover, the influence of monomer and initiator concentrations and polymerization temperature on the rate of polymerization (R_p) were investigated.

EXPERIMENTAL

Furfurylamine (Merck, 98 %), triethylamine (Aldrich, 99 %), acryloyl chloride (Merck, 99 %) and toluene (Merck, 99 %) were used without further purification. Dichloromethane (Fluka, 99 %) was distilled in the presence of CaH_2. Benzoyl peroxide (Merck) was purified by recrystallization from chloroform. The monomer synthesis was monitored by TLC and UV-Lamp. The monomer was purified by flash column chromatography with Merck silica gel 5554.

IR spectra were recorded with JASCO FT-IR 480 plus spectrometer and selective peaks were reported. ^{1}H NMR and ^{13}C NMR were recorded with Bruker Spectroscopin Avance PDX 400 MHz using tetramethysilane (TMS) as standard.

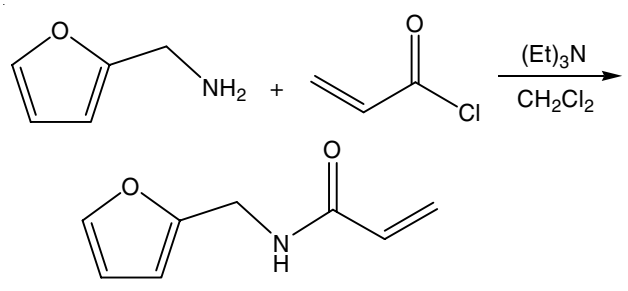
Preparation of *N*-[(furan-2-yl)methyl]acrylamide: 1.51 g (1.55×10^{-2} mol) furfurylamine and 2.35 g (2.32×10^{-2} mol) triethylamine were dissolved in dry dichloromethane (20 mL) and to this solution acryloyl chloride 1.40 g (1.55×10^{-2} mol) was added slowly at 0 °C (Fig. 1). The reaction mixture was stirred at room temperature for 20 h and the mixture was quenched with saturated solution of NH_4Cl and extracted 3 times with CH_2Cl_2 (total 50 mL). The combined organic phase was

dried with Na_2SO_4 and concentrated under reduced pressure. Upon purification with flash column (hexane:ethyl acetate, 5:1), the product was isolated (1.64 g, 70 % yield). ^{1}H NMR (δ, TMS): 7.32-7.23 (m, 1H), 6.31-6.19 (m, 2H), 6.16 (d, *J* = 3.2 Hz, 1H), 6.09-5.89 (m, 2H), 5.62-5.54 (m, 1H), 4.42 (d, *J* = 5.6 Hz, 2H). ^{13}C NMR (δ, TMS): 162.95, 149.41, 140.28, 128.25, 125.08, 108.70, 105.80, 34.70. FTIR (KBr, cm^{-1}): 3341 (N–H stretching); 3114 and 3070 (=C–H stretching); 2951 and 2919 (C–H stretching); 1658 (C=O stretching); 1620 (C=C stretching); 1549, 1407, 1309, 1241, 1197, 1146, 1073, 987, 968, 920, 875, 753, 596.

Polymerization technique: A typical polymerization procedure is as follows; *N*-[(furan-2-yl)methyl]acrylamide (0.2 g, 20.7 × 10^{-2} mol) and benzoyl peroxide (0.05 g, 1.43 × 10^{-2} mol) were dissolved 10 mL of toluene in a 25 mL double-neck round bottom flask. After nitrogen was filled into the flask, the polymerization was initiated by heating at 90 °C in an oil bath with a magnetic stirrer. During heating, insoluble part of polymer was precipitated and thereafter collected by filtration. The soluble part was precipated in hexane. The reaction products were partly soluble in common organic solvents (chloroform, dimethyl sulfoxide, tetrahydrofuran *etc.*). The obtained polymers were dried under vacuum at room temperature for an overnight. The conversion of monomer to polymer was measured by gravimetry.

RESULTS AND DISCUSSION

A novel acrylamide monomer of *N*-[(furan-2-yl)methyl]-acrylamide was prepared starting from furfurylamine (**Scheme-I**) and structure was confirmed by ^{1}H NMR (Fig. 1a), ^{13}C NMR and FTIR (Fig. 2a) analyses. In ^{1}H NMR, olefinic and aromatic protons were appeared in down fields (5.54-7.32 ppm) as expected. The methylene signals were observed at 4.42 ppm as multiplet. The existence of carbonyl group was detected at 162 ppm in ^{13}C NMR and 1658 cm^{-1} in FTIR spectrum. The NMR spectrum of the poly *N*-[(furan-2-yl)methyl]acrylamide (Fig. 1b) shows clearly furan protons between the range of 6.7-7.1 ppm, where there is no any other signal corresponding to olefinic protons. The methylene signals were appeared in 4.42 ppm similar to the NMR of monomer (Fig. 1a).



Scheme-I: Preparation of *N*-[(furan-2-yl)methyl]acrylamide monomer

The polymerization of *N*-[(furan-2-yl)methyl]acrylamide in toluene, using benzoyl peroxide as an initiator was carried out under an inert atmosphere of nitrogen in polymerization tubes. The precipitated polymer was collected by filtration and the soluble part of the polymer was precipitated in non-polar organic solvents.

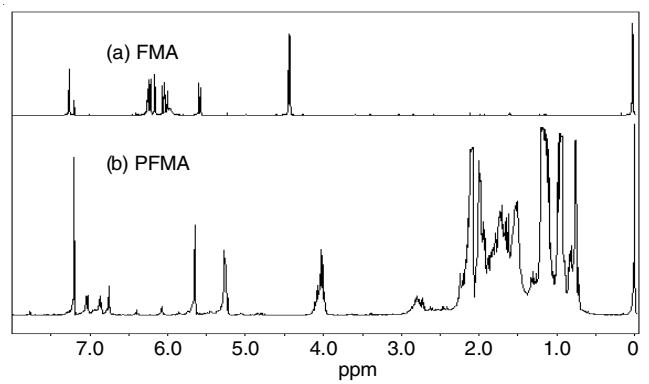


Fig. 1. ^{1}H NMR spectra of: (a) *N*-[(furan-2-yl)methyl]acrylamide (FMA), (b) poly*N*-[(furan-2-yl)methyl]acrylamide (PFMA)

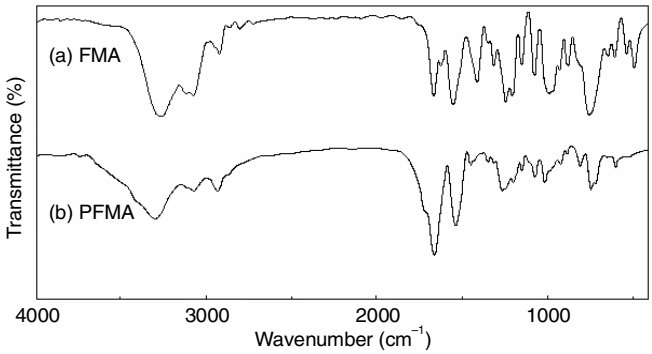
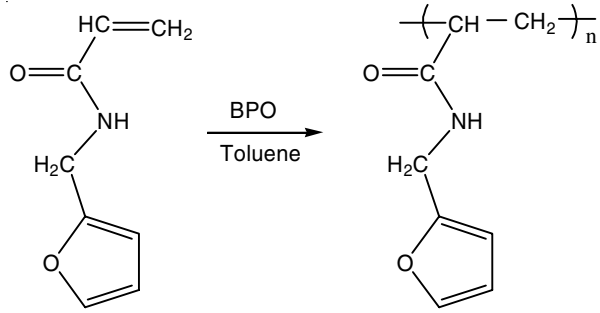


Fig. 2. FT-IR spectra of: (a) *N*-[(furan-2-yl)methyl]acrylamide (FMA), (b) poly *N*-[(furan-2-yl)methyl]acrylamide (PFMA)

The IR spectra confirmed the chemical structures, exhibiting all the absorption bands attributable to the functional groups comprising the polymer. The FTIR spectra of the prepared polymer reveals disappearance of the band at 1620 cm^{-1} due to being the olefinic C=C stretching, verifying the polymerization of *N*-[(furan-2-yl)methyl]acrylamide. FTIR absorption bands resulting from C=O stretching of amide was conspicuously occurred at 1681 cm^{-1} in poly *N*-[(furan-2-yl)-methyl]acrylamide (PFMA). In polymer spectrum, the band appearing at 3294 cm^{-1} is clearly belongs to N-H stretching. On the basis of the analyses conducted, the structure of polymer was accepted as given in **Scheme-II**.



Scheme-II: Polymerization of *N*-[(furan-2-yl)methyl]acrylamide

Kinetics of polymerization of *N*-[(furan-2-yl)methyl]acrylamide

Effect of initiator and monomer concentration on the rate of polymerization of *N*-[(furan-2-yl)methyl]acrylamide: Polymer unable to obtain under experimental when benzoyl

peroxide concentration was less than 3.4×10^{-3} mol L^{-1}. Therefore, the effect of initiator concentration on the polymerization rate was studied for initiator concentrations of 3.4×10^{-3}, 6.9×10^{-3}, 1.38×10^{-2} and 2.07×10^{-2} mol L^{-1} with monomer concentration constant at 4.42×10^{-1} mol L^{-1} (Table-1). The polymerization starts without any induction period. The rate of polymerization (R_p) was calculated from the slope of percentage conversion *versus* time plots, at low conversion. The data demonstrates that the R_p increases with the increase in benzoyl peroxide concentration and this explains the increase in the radical concentration in the reaction media. The initiator exponent, calculated from the slope of ln R_p *versus* ln [BPO], is 0.51 (Fig. 3).

TABLE-1
EFFECT OF [BPO] ON POLYMERIZATION

S. No.	[BPO] × 10^3 (mol/L)	Conversion (%)	$R_p \times 10^4$ (mol/Ls)
1	3.4	6.0	3.6
2	6.9	7.9	5.2
3	13.8	9.4	7.1
4	20.7	14.7	9.0

[FMAA] = 4.42×10^{-1} mol/L, temperature = 90 °C, time = 4 h

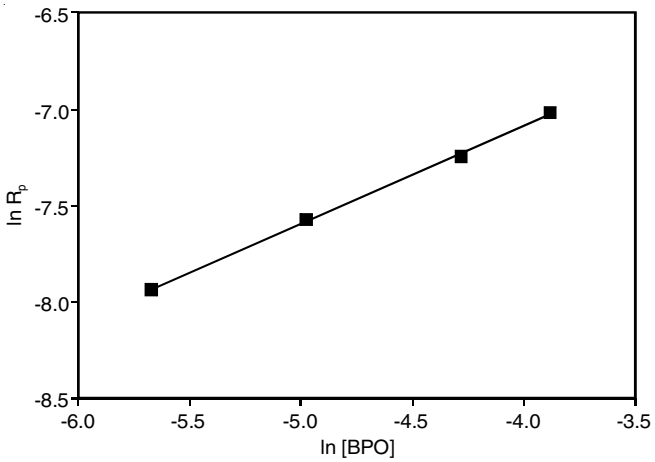


Fig. 3. Variation of ln R_p with ln [BPO] and fixed [FMA] = 4.42×10^{-1} mol/L at 90 °C

The effect of *N*-[(furan-2-yl)methyl]acrylamide concentration on the polymerization rate was studied for monomer concentrations of 8.8×10^{-2}, 11.0×10^{-2}, 11.9×10^{-2} and 13.2×10^{-2} mol L^{-1} (Table-2). The initiator concentration was held at constant value, being 2.07×10^{-2} mol L^{-1}. Fig. 4 demonstrates the conversion *versus* polymerization time in different monomer concentration. The polymerization rate for each initial monomer concentration, R_p, was obtained from the slopes of the linear part of conversion *versus* time plots. The rate of polymerization (R_p) increases linearly with the initial monomer concentration (Fig. 5). The polymerization rate is faster at the first hour and the conversion increases with increasing monomer concentrations (Fig. 4). The monomer exponent, calculated from the slope of ln R_p *versus* ln [FMA], is 1.69 (Fig. 5). Consequently, the polymerization rate equation is $R_p = k[M]^{0.51}[I]^{1.69}$. This result indicates that termination occurs through bimolecular interaction of growing chain radicals [23,24].

TABLE-2
EFFECT OF [FMA] ON POLYMERIZATION

S. No.	[FMA] × 10^2 (mol/L)	Conversion (%)	$R_p \times 10^4$ (mol/Ls)
1	8.8	37.3	10.4
2	11.0	40.1	14.2
3	11.9	43.2	16.5
4	13.2	45.7	21.0

[BPO] = 20.7×10^{-3} mol/L, temperature = 90 °C, time = 4 h

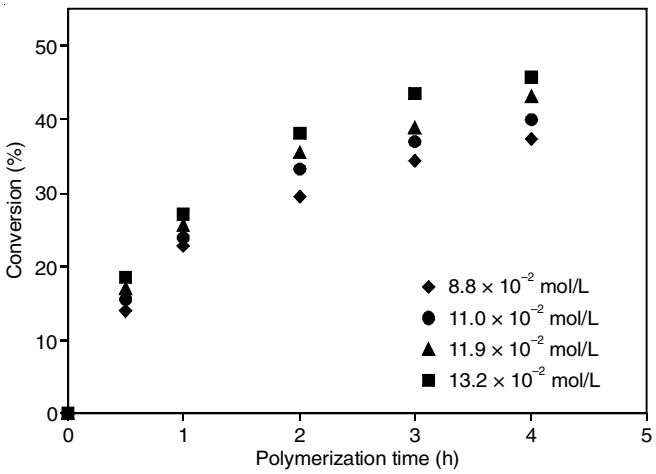


Fig. 4. Effect of the monomer concentration on the conversion. [BPO] = 20.7×10^{-3} mol/L at 90°C

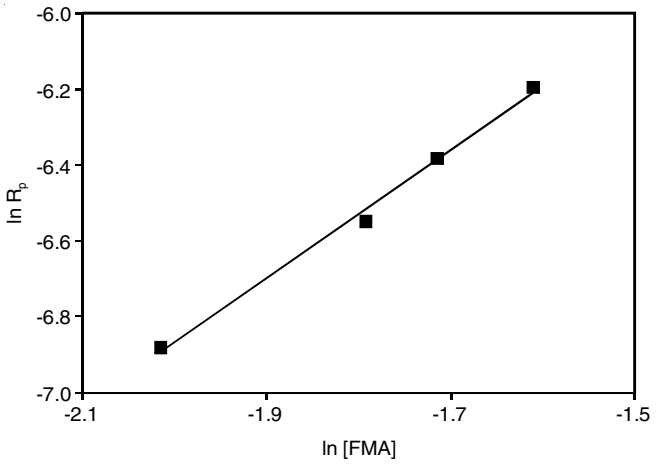


Fig. 5. Variation of ln R_p with ln [FMA] and fixed [BPO] = 20.7×10^{-3} mol/L at 90 °C

Effect of polymerization temperature: The polymerization reactions were carried out at different temperatures (70, 80 and 90 °C) at fixed concentrations of benzoyl peroxide (2.07×10^{-2} mol L^{-1}) and *N*-[(furan-2-yl)methyl]acrylamide (1.32×10^{-1} mol L^{-1}). Figs. 6 and 7 illustrate that the polymerization rate is strongly dependent on the polymerization temperature. The polymerization rate increases with rising temperature (Fig. 6). Arrhenius activation energy, calculated from the slope of the plot ln R_p *vs.* 1/T(Fig. 7), is 84 kJ mol^{-1}.

Conclusion

New acrylamide monomer containing a furan side group was synthesized and polymerized by means of free radical polymerization. The dependence of initiator and monomer concentration on polymerization rate pursued the classical

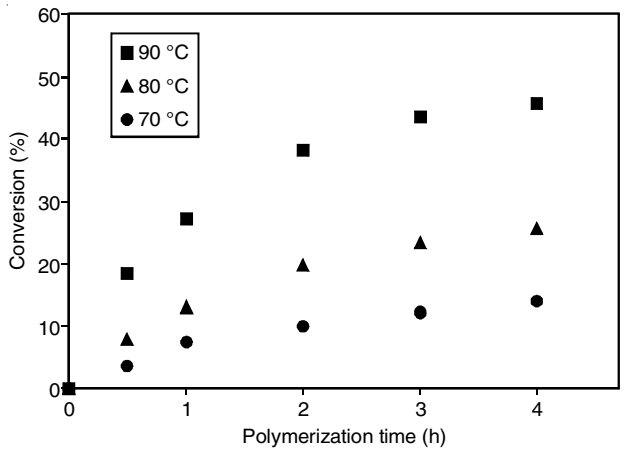


Fig. 6. Effect of the polymerization temperature on the conversion of *N*-[(furan-2-yl)methyl]acrylamide. [FMA] = 4.42 × 10^{-1} mol/L and [BPO] = 20.7 × 10^{-3} mol/L

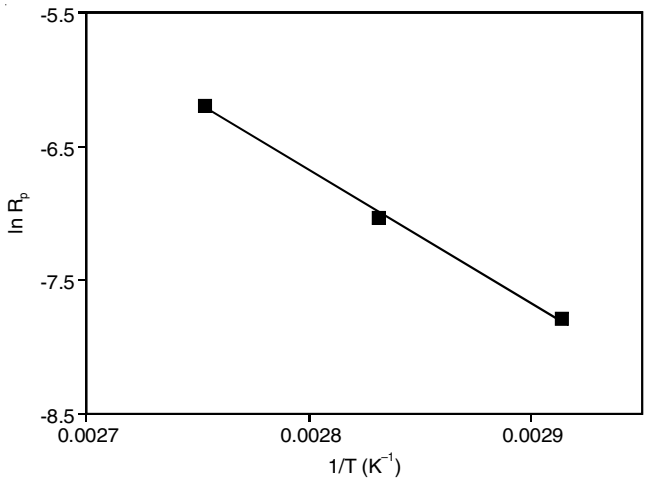


Fig. 7. Plot of ln R_p *versus* 1/T. [FMA]= 4.42 × 10^{-1} mol/L and [BPO]= 20.7 × 10^{-3} mol/L

kinetic theory. Due to the fact that the polymer obtained incorporates several functional groups (*i.e.* carbonyl, furan and amide) in modified polymers is attainable. The biological activity studies of poly *N*-[(furan-2-yl)methyl]acrylamide are in progress and will be reported in due course.

REFERENCES

1. X. Chen, M.A. Dam, K. Ono, A. Mal, H. Shen, S.R. Nutt, K. Sheran and F. Wudl, *Science*, **295**, 1698 (2002).
2. H. Laita, S. Boufi and A. Gandini, *Eur. Polym. J.*, **33**, 1203 (1997).
3. A. Gandini, *Polym. Chem.*, **1**, 245 (2010).
4. M. Shi and M.S. Shoichet, *J. Biomater. Sci. Polym. Ed.*, **19**, 1143 (2008).
5. S. Kantevari, T. Yempala, G. Surineni, B. Sridhar, P. Yogeeswari and D. Sriram, *Eur. J. Med. Chem.*, **46**, 4827 (2011).
6. M. Shi, K. Ho, A. Keating and M.S. Shoichet, *Adv. Funct. Mater.*, **19**, 1689 (2009).
7. H. Liu, B. Lepoittevin, C. Roddier, V. Guerineau, L. Bech, J.-M. Herry, M.-N. Bellon-Fontaine and P. Roger, *Polymer*, **52**, 1908 (2011).
8. M.Z. Elsabee, E.A. Ali, S.M. Mokhtar and M. Eweis, *React. Funct. Polym.*, **71**, 1187 (2011).
9. N. Sibold, P.J. Madec, S. Masson and T.N. Pham, *Polymer*, **43**, 7257 (2002).
10. R. Ribic, L. Habjanec, M. Brgles, S. Tomic and J. Tomasic, *Bioorg. Med. Chem.*, **17**, 6096 (2009).
11. C. Song, L. Li, F. Wang, J. Deng and W. Yang, *Polym. Chem.*, **2**, 2825 (2011).
12. A.M. Atta, H.S. Ismail and A.M. Elsaaed, *J. Appl. Polym. Sci.*, **123**, 2500 (2012).
13. T. Singh and R. Singhal, *J. Appl. Polym. Sci.*, **125**, 1267 (2012).
14. Z. Liu, M. Cardosi, J. Rodgers, G. Lillie and L. Simpson, *React. Funct. Polym.*, **70**, 715 (2010).
15. H.M. Li, J. Zhuang, H.B. Liu, L. Feng and W. Dong, *Polym. Eng. Sci.*, **52**, 431 (2012).
16. M. Liu, J. Chen, Y.P. Cheng, Y.N. Xue, R.X. Zhuo and S.W. Huang, *Macromol. Biosci.*, **10**, 384 (2010).
17. J.I. Ngadaonye, L.M. Geever, M.O. Cloonan and C.L. Higginbotham, *J. Polym. Res.*, **19**, 9822 (2012).
18. B. Singh, G.S. Chauhan, S. Kumar and N. Chauhan, *Carbohydr. Polym.*, **67**, 190 (2007).
19. P.A. Kavakli, C. Uzun and O. Guven, *React. Funct. Polym.*, **61**, 245 (2004).
20. F.A. Al-Sagheer, A.A.M. Ali, M.A. Reyad and M.Z. Elsabee, *Polym. Int.*, **44**, 88 (1997).
21. A.Z. El-Sonbati, M.A. Diab and R.H. Mohamed, *Polym. Int.*, **60**, 1467 (2011).
22. M. Solener, *J. Appl. Polym. Sci.*, **109**, 1461 (2008).
23. C.H. Bamford and E. Schofield, *Polymer*, **24**, 433 (1983).
24. K. Behari, K. Taunk and R. Das, *Polym. Int.*, **46**, 126 (1998).