ISSN : 0974 - 7478 Volume 8 Issue 1

Trade Science Inc.

Macromolecules

An Indian Journal

Full Paper

MMAIJ, 8(1), 2012 [7-11]

Co-polycondensation of 4-(4-Phthalimidophenyl)-1,2,4-triazolidin-3,5-dion and 4-(4-Nitrophenyl)-1,2,4-triazolidin-3,5-dion with Diisocyanates

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Received: 27th December, 2011 ; Accepted: 12th January, 2012

ABSTRACT

4-(4-Nitrophenyl)urazole(4) was reacted with two equivalents of hexamethylene diisocyanate (HMDI)(5), isophorone diisocyanate (IPDI)(6) and tolylene-2,4-diisocyanate (TDI)(7), in DMF as a solvent to forming the related diisocyanates. The reaction of 4-(4-aminophenyl)urazole(1) with phthalic anhydride(2) in a mixture of pyridine and acetic acid (2:3) as a solvent led to the related amic acid. The amic acid was heated in the same solvent mixture to give 4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione(3). Solution polyconden-sation reactions of the new diisocyanates, with 4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione(3) were performed in DMF in the presence of pyridine as a catalyst and lead to the formation of novel aliphatic and aromatic co-polyureas(8, 9, 10). These novel co-polyureas have inherent viscosities in a range of 0.11-0.23 dLg^{-1} in DMF at 25°C. Some structural characterization and physical properties of these novel co-polymers are reported.

KEYWORDS

4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione;
Step-growth polymerization;
Co-polyurea;
4-(4-nitrophenyl)-1,2,4-triazolidine-3,5-dione,
Urazole.

INTRODUCTION

Urazoles(1,2,4-triazolidine-3,5-diones) are very significant chemical reagents in the laboratory as well as in industry. Industrially urazoles are used as a stabilizer in milk, and in the production of anti-tumor drugs[1]. They are also utilized in polymeric materials[2, 3], in the production of automobile air bags, as a blowing agent in plastics, in the manufacture of antifungal compounds, and herbicides[4]. Urazoles have been used as a laboratory reagent for preparation of novel organometallic and heterocyclic compounds[5]; for example triazolo[1,2-a]indazole-triones have been prepared via a three-component method, by using homogeneous[6], or heterogeneous[7] catalysts. Some urazole derivatives were found to be potent cytotoxic agents in murrain and human cancer cell lines. Other pharmaceutical properties of urazole derivatives are hypolipidemic activity via lowering serum, cholesterol, and triglyceride levels[8], pesticides[9] and insecticides[10]. Preparations of thermoplastics, production of heat resistant coatings[11], tire rubbers with high gripability[12] and melamine resins[13], are among the applications in the field of polymerization of urazole derivatives. Urazoles could also be oxidized to the corresponding triazolinedione derivatives using various oxidizing reagents such as silica chloride/$NaNO_2$[14], silica sulfuric acid/$NaNO_2$[15], Ph_3BiCO_3[16], $KMnO_4/Al_2O_3$[17], 1,4-diazabicyclo[2.2.2]octane, 1,4-bis(oxide)-bis(hydrogen peroxide)/MCl[18], NO^+crown $H(NO_3)_2^-$[19], $Ca(OCl)_2$[20], $K_2Cr_2O_7/AlCl_3$[21], silica sulfuric acid/$KClO_3$[22], silica chloride/oxone[22], 1,3-dihalo-5,5-dimethylhydantoin[23], periodic acid, and oxone®/KBr[24]. The resulted products of these reactions, triazolinediones, are very active species toward cycloaddition and ene reactions[25-27]. Triazolinediones, also used as an initiator in the radical addition reactions[28].

The synthesis and characterization of the macromolecules restrain heterocyclic rings in the main chain has been the topic of considerable interest, because of their relatively good thermal stability and some attractive novel properties[29].

EXPERIMENTAL

Apparatus

Proton nuclear magnetic resonance ^{1}HNMR spectra were recorded on a 500 MHz Bruker Advance DRX instrument using DMSO-d_6 as solvent and tetramehyl silane as an internal standard, Peak multiplicities are assigned as singlet(s), doublet(d), triplet(t), and multiplet (m). IR spectra were recorded on Shimadzu 470 IR spectrophotometer. Spectra of solids were carried out using KBr disks. Vibrational transition frequencies are reported in wave number(cm^{-1}). Band intensities are assigned as weak(w), medium(m), shoulder(sh), strong(s) and broad(br). Inherent viscosities were measured by a standard procedure using a Cannon Fensk Routine Viscometer. Thermal gravimetric analysis(TGA) data for polymers were taken by Amir-Kabir University, Tehran, Iran, in nitrogen atmosphere at a rate of 10°C/min. Elemental analyses were performed by Ferdossi University, Mashhad, Iran.

Reagents and monomer

Reagents were purchased from Fluka Chemical Co. and Merk Co. 4-(4-nitrophenyl)urazole and 4-(4-aminophenyl)urazole were synthesized according to our previous report[30].

Preparation of 4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3)

In a 25 mL round bottom flask, was placed 4-(4-aminophenyl)-1,2,4-triazolidine-3,5-dione(1) (0.200 g, $1.04*10^{-3}$ mol), phthalic anhydride(2) (0.15 g, $1.04*10^{-3}$ mol) and a mixture of acetic acid and pyridine(AcOH:Py=3:2) as solvent. The reaction mixture was stirred for 24 h in room temperature, then refluxed for 8 h. The white solid was filtrated off, and washed with hot ethanol; (0.46 g, 76%); mp 363-365°C. IR(KBr): 3200(w), 3100(m), 2800(w), 176 (w), 1700(s, br), 1520(s), 1460(s), 1380(s), 1290 (m), 1220(m, sh), 1160(w), 1120(s), 1080(s), 880(s), 840(s), 790(m, sh), 770(m), 720 (s), 680(s), 660(m), 530(s) cm^{-1}. ^{1}H-NMR(DMSO-d_6, TMS): 10.57(s, 2H, br), 8.00 (m, 2H, J=10 Hz), 7.93 (m, 2H, J=10 Hz), 7.63(d, 2H, J=10 Hz), 7.58(d, 2H, J=10 Hz) ppm. ANAL. Calcd for $C_{16}H_{10}N_4O_4$: C, 56.38%; H, 3.38%; N, 18.79%. Found: C, 56.50%; H, 3.12%; N, 19.00%.

Co-polymerization of 4-(4-nitrophenyl)urazole (4) and 4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) with hexamethylene diisocyanate

In a 10 mL round bottom flask, 4-(4-nitrophenyl) urazole(4) (0.1430 g, $6.47*10^{-4}$ mol) was added to a solution of hexamethylene diisocyanate(5) (0.2178 g, $1.29*10^{-3}$ mol) and pyridine (1 drop) in 1 mL of N,N-dimethylformamide(DMF). The solution was stirred for 24 h in room temperature. 4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione(7) (0.1931 g, $6.47*10^{-4}$ mol) was added and the solution was stirred for 24 h in 40°C, then for 8 h in 55°C. 0.5 mL of DMF was added and the solution was stirred for additional 24 h in 80°C. The viscose gel was precipitated in 50 mL of methanol. The off-white solid(0.40 g, 70%) was filtrated. mp 230-233°C. Inherent viscosity (0.5 g/dL DMF, 25°C) =0.55 dLg^{-1}. Thermal analysis: T_5 215°C, T_{10} 230°C. Carbon yield(600°C) 0%; IR(KBr): 3300(m), 3100(m), 2900(m), 1730(s, br), 1620 (m), 1520(s), 1420(m), 1380(s), 720(m), 535(w) cm^{-1}. ANAL. Calcd for $C_{40}H_{40}N_{12}O_{12}$: C, 54.54%; H, 4.58%; N, 19.08%. Found: C, 53.65%; H, 5.12%; N, 18.49%.

Co-polymerization of 4-(4-nitrophenyl)urazole (4) and 4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) with isophorone diisocyanate

In a 10 mL round bottom flask, 4-(4-nitrophenyl) urazole(4) (0.1612 g, 7.26*10^{-4} mol) was added to a solution of isophorone diisocyanate(6) (0.3232 g, 1.45*10^{-3} mol) and pyridine(1 drop) in 1 mL of N,N-dimethylformamide(DMF). The solution was stirred for 24 h in room temperature. 4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione(3) (0.2161 g, 7.26*10^{-4} mol) was added and the solution was stirred for 24 h in room temperature, then for 24 h in 60 °C. 0.5 mL of DMF was added and the solution was stirred for additional 24 h in 90°C. The viscose gel was precipitated in 50 mL of methanol. The off-white solid (0.59 g, 82%) was filtrated. mp 332-334°C. Inherent viscosity(0.5 g/dL DMF, 25°C) =0.40 dLg^{-1}. Thermal analysis: T_5 220°C, T_{10} 233°C. Carbon yield(600°C) 3%; IR(KBr): 3400(w), 3200(w), 3100(m), 2900(w, sh), 1700-1780(m, br), 1680(w), 1540(m), 1520(s), 1480(m), 1380(s), 1120(s), 1080 (s), 880(s), 840(s), 780(s), 720(s), 530(s) cm^{-1}. ANAL. Calcd for $C_{48}H_{52}N_{12}O_{12}$: C, 58.29%; H, 5.30%; N, 16.99%. Found: C, 59.00%; H, 5.46%; N, 16.55%.

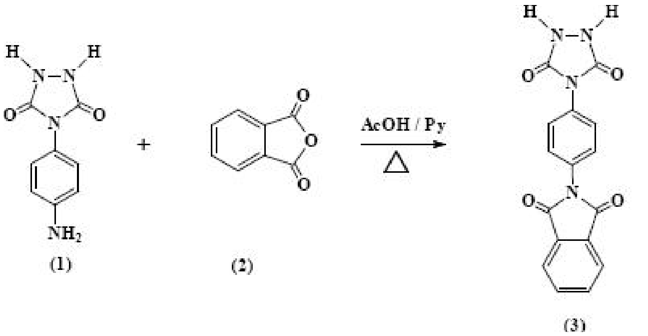
Co-polymerization of 4-(4-nitrophenyl)urazole (4) and 4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione (3) with tolylene diisocyanate

In a 10 mL round bottom flask, 4-(4-nitrophenyl) urazole(4) (0.1701 g, 7.66*10^{-4} mol) was added to a solution of tolylene diisocyanate(7) (0.2660 g, 1.53*10^{-3} mol) and pyridine (1 drop) in 1 mL of N,N-dimethylformamide (DMF). The solution was stirred for 24 h in room temperature. 4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione(3)(0.2282 g, 7.66*10^{-4} mol) was added and the solution was stirred for 12 h in 45 °C. 0.5 mL of DMF was added and the solution was stirred for 24 h in 60°C, then for 24 h in 80°C. The viscose gel was precipitated in 50 mL of methanol. The off-white solid(0.45 g, 66%) was filtrated. mp 330-335°C. Inherent viscosity(0.5 g/dL DMF, 25°C) =0.43 dLg^{-1}. Thermal analysis: T_5 233°C, T_{10} 250°C. Carbon yield (600°C) 6%; IR(KBr): 3300(w), 3100(w), 1780-1720(s, br), 1680(m), 1520(w), 1380 (s), 1220(m), 1110(s), 1080(s), 880(s), 840(m), 780(m, sh), 720(s), 680(w), 660(w), 530(s) cm^{-1}. ANAL. Calcd for $C_{42}H_{28}N_{12}O_{12}$: C, 56.50%; H, 3.16%; N, 18.83%. Found: C, 57.00%; H, 3.13%; N, 18.75%.

RESULTS AND DISCUSSION

Monomer synthesis

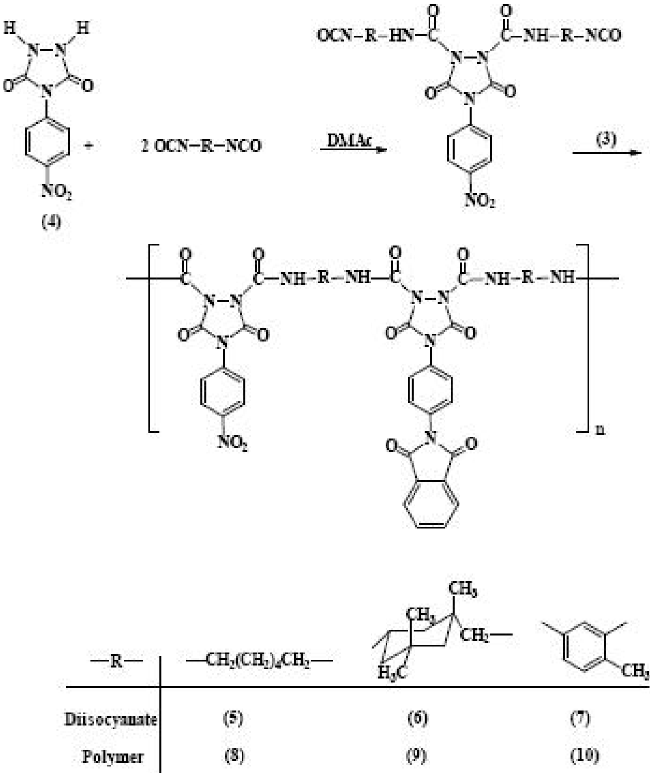
4-(4-Aminophenyl)-1,2,4-triazolidine-3,5-dione(1) was reacted with phthalic anhydride(2) in a mixture of pyridin/acetic acid (2:3) at room temperature. The resulted amic acid was heated to reflux for 8 hours, condensing to 4-(4-phthalimidophenyl)-1,2,4-triazolidine-3,5-dione(3), In high yield (Scheme 1).



The compound**(3)** was characterized by IR, ^{1}H-NMR and elemental analysis. The IR spectrum of**(3)** showed a peak at 3200 cm^{-1} for the stretching vibration of the N-H bonds, and a peak at 3100 cm^{-1} for stretching vibration of the aromatic C-H bonds. The strong peak at 1700 cm^{-1} covers the carbonyl related area of both the urazolic and imidic carbonyl groups. The strong peak at 1520 is related to stretching vibrations of the aromatic carbon-carbon double bonds. The ^{1}H-NMR spectrum of **(3)** showed a pair of doublets at 7.63 and 7.58 ppm for the aromatic protons of phenylene group. The two multiplet peaks appeared at 8.00 and 7.93 ppm are related to the aromatic protons which are in orto and meta positions relative to imide carbonyl groups of phthalimid moiety respectively. The broad peak related to the N-H protons is at 10.57 ppm. Elemental analysis results for carbon, hydrogen, and nitrogen is also in good agreement with the calculated amounts, thus confirm the structure of the compound**(3)**.

Polymerization reactions

Since various derivatives of 1,2,4-triazolidine-3,5-dione have been reacted with aliphatic and aromatic diisocyanates to produce related polyureas**[31]**, we decided to perform this type of reaction for the formation of the novel urazole containing co-polyureas. Thus HMDI(5), IPDI(6) and TDI(7) were selected as diisocyanates. The reaction of monomer(1) with two moles of these diisocyanates, then addition of monomer(3) was performed via solution polymerization. The reactions were carried out in DMF solution in the presence of pyridine as a catalyst and the resulted co-polyureas(8-10) were obtained as off-white solids in high yields (Scheme 2).



The resulting co-polymers were characterized by IR, elemental analysis, and TGA.

The IR spectrum of the co-polymer(8) showed a peak at 3300 cm^{-1} for stretching vibration of the amide N-H bounds, two peaks at 3100 and 2900 cm^{-1} for stretching vibration of the aromatic and aliphatic C-H bounds respectiely. The strong peak at 1730 and the medium one in 1620 cm^{-1} are the specific characteristic of the urazolic carbonyls, which cover the main chain carbonyl groups. The strong peak at 1520 is related to stretching vibrations of the aromatic carbon-carbon double bonds. The elemental analysis results also are in good agreement with the calculated percentages for carbon, hydrogen and nitrogen contents in co-polymer repeating unit.

The IR spectrum of the co-polymer(9) showed a peak at 3400 cm^{-1} for stretching vibrations of the amide N-H bonds. The peaks appeared at 3100 and 2900 cm^{-1} are attributed to stretching vibration of the aromatic C-H bounds and the aliphatic C-H bounds of the isophorone moiety, respectively. The peaks at 1780-1700, and 1680 cm^{-1} are the specific characteristic of the urazolic carbonyls which cover the main chain carbonyl groups. The strong peak at 1520 is related to stretching vibrations of the aromatic carbon-carbon double bonds. The elemental analysis results are in good agreement with the calculated percentages for carbon, hydrogen and nitrogen contents in co-polymer repeating unit.

The IR spectrum of the co-polymer(10) showed a peak at 3300 cm^{-1} for the stretching vibrations of the N-H bounds. The peak appeared at 3100 cm^{-1} is attributed to stretching vibration of the the aromatic C-H bounds. The strong peak at 1780-1720 and the medium one in 1680 cm^{-1} are the specific characteristic of the urazolic carbonyls which cover the main chain carbonyl groups. Also the strong peak at 1520 cm^{-1} is attributed to stretching vibrations of the aromatic carbon-carbon double bonds. The elemental analysis results are in good agreement with the calculated percentages for carbon, hydrogen and nitrogen contents in polymer repeating unit.

The co-polymers (8), (9) and (10) are soluble in polar organic solvents such as DMF, DMSO and DMAc, and are insoluble in solvents such as water, methanol, acetone, cyclohexane and chloroform.

Thermal properties

The thermal behavior of the co-polymers 8, 9 and 10 was measured by thermogravimetric analysis(TGA) at a rate of 10°C/min in nitrogen atmosphere. An examination of the data for the co-polymer 8 reveals that this co-polyurea is thermally stable up to 200°C in nitrogen atmosphere; This co-polymer shows 5% and 10% weight loss at 215 and 230°C respectively. The co-polymer 9 shows 5% weight loss at 220°C and 10% weight loss at 233 °C. Also an examination of the data for the co-polymer 10 shows that this co-polyurea shows 5% and 10% weight loss at 233 and 250°C respectively.

CONCLUSIONS

This investigation has shown that 4-(4-nitrophenyl)

1,2,4-triazolidine-3,5-dione (1) and 4-(4-phthalimidophenyl)urazole(3) are interesting monomers for the co-polycondensation reactions. These compounds can act as bifunctional monomers and their co-polymerization reaction with aliphatic and aromatic diisocyanates gave the novel co-polyureas(8-10).

ACKNOWLEDGMENTS

Financial support of this work from the Research Affairs Division, Shahrood University of Technology, Shahrood, I.R. Iran, is gratefully acknowledged.

REFERENCES

[1] I.H.Hall, O.T.Wong, R.Simlot, M.C.Miller, R.Izydore; Anticancer.Res., **12**, 1355-1362 **(1992).**

[2] S.Mallakpour, Z.Rafiee; Polym.Bull., **56**, 293-303 **(2006).**

[3] S.Mallakpour, Z.Rafiee; J.Appl.Polym.Sci., **103**, 947-54 **(2007).**

[4] T.Jikihara, K.Matsuya, H.Ohta, S.Suzuki, O.Wakabayashi; US Patent, **4**, 249, 934 (**1981**); Jpn.Chem.Abstr., **95**, 62219y **(1981).**

[5] A.M.Boldi, C.E.Johnson, H.O.Eissa; Tet.Lett., **40**, 619-22 **(1999).**

[6] A.Bazgir, M.Seyyedhamzeh, Z.Yasaei, P.Mirzaei; Tet.Lett., **48**, 8790-8794 **(2007).**

[7] M.Adharvana Chari, G.Karthikeyan, A.Pandurangan, T.Siddulu Naidu, B.Sathyaseelan, S.M.Javaid Zaidi, A.Vinu; Tet.Lett., **51**, 2629-2632 **(2010).**

[8] R.A.Izydore, I.H.Hall; US Patent, **4**, 866,058 (1990); Chem.Abstr., **112**, 151876x **(1990).**

[9] D.Ovadia, N.Peleg, P.Bracha; US Patent, **4**, 087, 534 **(1978)**; Chem.Abstr., **89**, 109513h **(1978).**

[10] B.Von Bredow, H.Brechbuehler; Ger.Offen., **2**, 343, 347 **(1974)**; Chem.Abstr., **80**, 140210s **(1974).**

[11] H.Giesecke, R.Merten, L.Rottmaier; Ger.Offen., **3**, 027, 612 **(1982)**; Chem.Abstr., **96**, 182879f **(1982).**

[12] M.Oikawa, C.Ebina, N.Inui, H.Nagasaki, S.Yago; JP., **04**, 249, 552 **(1993)**; Chem.Abstr., **118**, 61373a **(1993).**

[13] L.Rottmaier, R.Merten; Ger.Offen., **3**,106, 944 **(1982)**; Chem.Abstr., **97**, 198209u **(1982).**

[14] M.A.Zolfigol, M.Torabi, S.E.Mallakpour; Tetrahedron., **57**, 8381-8384 **(2001).**

[15] M.A.Zolfigol, G.Chehardoli, S.E.Mallakpour; Synthetic Communications, **33**, 833-841 **(2003).**

[16] C.Me´nard, E.Doris, C.Mioskowski; Tetrahedron Letters, **44(5),** 6591-6593 **(2003).**

[17] A.R.Hajipour, S.E.Mallakpour, M.A.Zolfigol, H.Adibi; Indian J.Chem.Sec.B, **41(11),** 2425-2427 **(2002).**

[18] M.A.Zolfigol, P.Salehi, S.E.Mallakpour, M.Torabi; Bull.Chem.Soc.Jpn., **76(8)**, 1673-1674 **(2003).**

[19] M.A.Zolfigol, M.H.Zebarjadian, G.Chehardoli, S.E.Mallakpour, M.Shamsipur; Tetrahedron, **57**, 1627-1629 **(2001).**

[20] M.A.Zolfigol, S.Mallakpour, A.Khazaiae, R.G.Vaghaie, M.Torabi; Bull.Korean Chem.Soc., **25(8),** 1251-1252 **(2004).**

[21] I.Mohammadpoor-Baltork, M.M.Sadeghi, S.E.Mallakpour, A.R.Hajipour, H.Adibi; Synthetic Communications, **32(22),** 3445-3448 **(2002).**

[22] M.A.Zolfigol, M.H.Zebarjadian, M.Bagherzadeh, S.E.Mallakpour, G.Chehardoli, E.Kolvari, A.C.Ghorbani, N.Koukabi; Catalysis Communications, **8**, 256-260 **(2007).**

[23] M.A.Zolfigol, H.Nasr-Isfahani, S.Mallakpour, M.Safaiee; Synlett., **5**, 761-764 **(2005).**

[24] M.A.Zolfigol, M.Bagherzadeh, S.E.Mallakpour, G.Chehardoli, A.C.Ghorbani, N.Koukabi, M.Dehghanian, M.Doroudgar; Journal of Molecular Catalysis, **270**, 219-224 **(2007).**

[25] M.Alajarin, B.Bonillo, M.Marin-Luna, A.Vidal, R.J.Orenes; Org.Chem., **74**, 3558-3561 **(2009).**

[26] R.T.Dey, T.K.J.Sarkar; Org.Chem., **75**, 4521-4529 **(2010).**

[27] M.M.Roubelakis, G.C.Vougioukalakis, Y.S.Angelis, M.Orfanopoulos; Org.Lett., **8(1),** 39-42 **(2006).**

[28] G.Nicolaou, Y.Elemes; Tetrahedron Letters, **49**, 6324-6326 **(2008).**

[29] B.D.Sarwade, P.P.Wadgaonkar, S.S.J.Mahajan; Polym.Sci.Part A: Polym.Chem., **27**, 3263-3269 **(1989).**

[30] S.E.Mallakpour, H.Nasr-Isfahani; Indian Journal of Chemistry, **41B**, 169-174 **(2002).**

[31] **(a)** S.E.Mallakpour, H.Nasr-Isfahani; Polymer Science A, **43**, 1907-1912 **(2001)**; **(b)** S.E.Mallakpour, H.Nasr-Isfahani; Iranian Polymer Journal, **10**, 107-114 **(2001)**; **(c)** S.E.Mallakpour, H.Nasr-Isfahani; Polymer Science B, **43**, 105-111 **(2001)**; **(d)** S.E.Mallakpour, H.Nasr-Isfahani; Journal of Applied Polymer Science, **82**, 3177-3183 **(2001)**; **(e)** S.E.Mallakpour, H.Nasr-Isfahani; Iranian Polymer Journal, **11**, 57-61 **(2002).**