

Synthesis, Characterization, and Free Radical Polymerization of New Acrylamide-Based Monomer Containing a 1*H*-Tetrazole Ring: Thermal Investigation and Derivatization of the Homopolymer*

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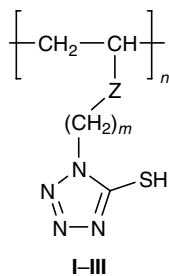
Abstract—*N*-[4-(1*H*-Tetrazol-5-yloxy)phenyl]acrylamide was synthesized and subjected to homopolymerization under radical initiation. The structure of the monomer and homopolymer was characterized by elemental analyses (C, H, N), FT-IR, and ¹³C and ¹H NMR data. Thermal behavior of the homopolymer was studied by differential scanning calorimetry and thermogravimetric analysis. The tetrazole ring in the homopolymer was converted into imidoil azide derivatives via reactions with cyanogen bromide, *p*-toluenesulfonyl chloride, and trifluoro-methanesulfonyl chloride.

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There are numerous reports on the addition, polymerization, and copolymerization of tetrazole-containing monomers, mainly under conditions of radical initiation. These polymers and copolymers have found many applications in various fields. For example, polymers obtained from 1-methyl- and 2-methyl-5-vinyl-tetrazole are suitable as components of clean slow-burning gas-generating compositions, strongly adherent math squib bridge wires [1, 2], and binders for explosive compositions [3, 4]. Polymeric derivatives of tetrazole-5-thiols and their metal and ammonium salts are widely used in photographic gelatins [5, 6]. For example, Grasshoff et al. [7] used polymers **I–III** in

combination with silver halide photographic elements as interlayers to provide interimage control, dispersants for dye image-forming materials, and silver scavengers.

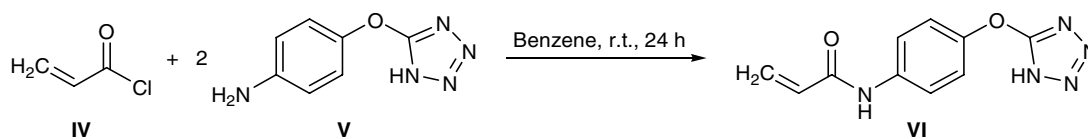
Stille and co-workers [8–11] reported on the preparation of 2-phenyl-5-(4-vinylphenyl)tetrazole, a polymer based thereon, and copolymers with various vinyl monomers and calculated the monomer reactivity ratio. 5-Vinyltetrazole polymers and copolymers are physiologically important; they exhibit anticoagulant activity via increase of the plasma recalcification time by prolonging the thrombin and thromboplastin times [12]. Analogous activity was revealed for poly(5-isopropenyltetrazole) [13, 14]. Tetrazole-containing polymers also show immunological and antitumor activity [15]. Their polyelectrolyte properties and the ability to form complexes with transition metal ions are used to prepare hydrogenation catalysts [16, 17]. Tetrazoles constitute a very important class of compounds in medical chemistry. Substituted tetrazoles were reported to exhibit a broad spectrum of neurological activity; depending on the substitution pattern, it ranges from strong stimulation of the nervous system to depressant action. Tetrazoles are also used as carboxylic acid pharmacophores in the design of anticancer, antimicrobial, antihypertensive, and antiallergic agents.



I, Z = *p*-C₆H₄, *m* = 1, *n* ≥ 100; **II**, Z = CONHC₆H₄-*m*, *m* = 0, *n* ≥ 100; **III**, Z = CONHMe₂CONHC₆H₄-*m*, *m* = 0, *n* ≥ 100.

* The text was submitted by the authors in English.

Scheme 1.



Tetrazole derivatives have recently attracted increased attention due to their industrial applications [18–30]. Kraft and co-workers recently reported on the synthesis and radical polymerization of *N*-(tetrazol-5-yl)-methacrylamide [31].

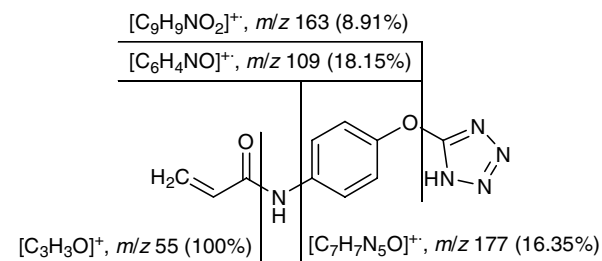
The goal of the present study was to synthesize, characterize, and examine the thermal behavior of a new polymer containing an aryloxy-(1*H*)-tetrazole pendant group. We also planned to develop procedures for the transformation of the tetrazole ring in the polymer to imidoyl azides and other important tetrazole derivatives.

The monomer, *N*-[4-(1*H*-tetrazol-5-yloxy)phenyl]-acrylamide (**VI**) was readily synthesized by one-pot reaction of acryloyl chloride (**IV**) with 4-(1*H*-tetrazol-5-yloxy)aniline (**V**) (Scheme 1). The reaction was carried out using 2 equiv of the amine, 1 equiv of which acted as base; excess aniline **V** was readily removed by stirring with 30% HCl before filtration. Monomer **VI** was fully characterized by the ^1H and ^{13}C NMR, FT-IR (Figs. 1, 2), and mass spectra. The ^{13}C NMR spectrum of **VI** clearly confirmed its purity. Scheme 2 shows the fragmentation pattern of compound **VI** under electron impact.

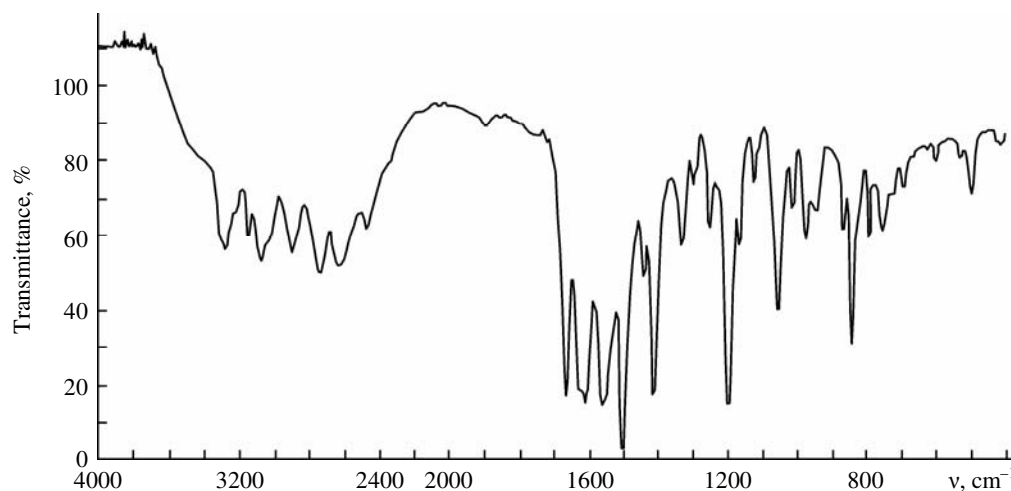
Polymerization of **VI** in DMF at 85°C gave a polymeric material (Scheme 3) with a high intrinsic viscosity, $\eta_{\text{int}} = 1.47$ g dl (0.050 g, 10 ml of DMF, 24°C).

Homopolymer **VII** thus obtained had no sharp melting point. It is insoluble in most solvents, slightly soluble in boiling *p*-xylene and THF and in MeOH, DMF, and DMSO at room temperature, and soluble in boiling MeOH, DMF, and DMSO.

Scheme 2.



The ^1H NMR spectrum of **VII** is shown in Fig. 3. Due to hygroscopic properties of the polymer and the solvent (DMSO- d_6), a broad band corresponding to the tetrazole NH proton and absorbed water covers the region between δ 3.94 and 2.89 ppm. The isotactic (*mm*), syndiotactic (*rr*), and atactic (*mr*) sequences are assigned in Fig. 3b. The ^{13}C NMR and FT-IR spectra of **VII** were also obtained (Figs. 4, 5). Signals from eight nonequivalent carbon atoms are observed in the ^{13}C NMR spectra of monomer **VI** (Fig. 2) and homopolymer **VII** (Fig. 4). Disappearance of two vinylic carbon signals (δ_{C} 163.04 and 126.67 ppm in the spec-

Fig. 1. FT-IR spectrum (KBr) of monomer **VI**.

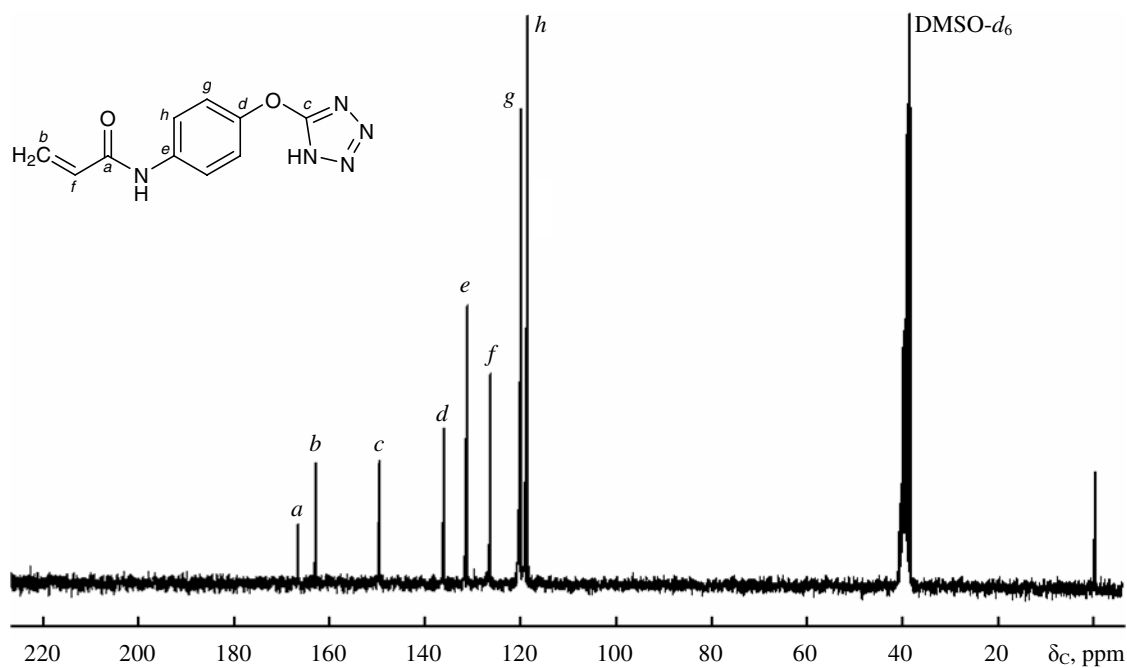


Fig. 2. ^{13}C NMR spectrum ($\text{DMSO}-d_6$) of monomer VI.

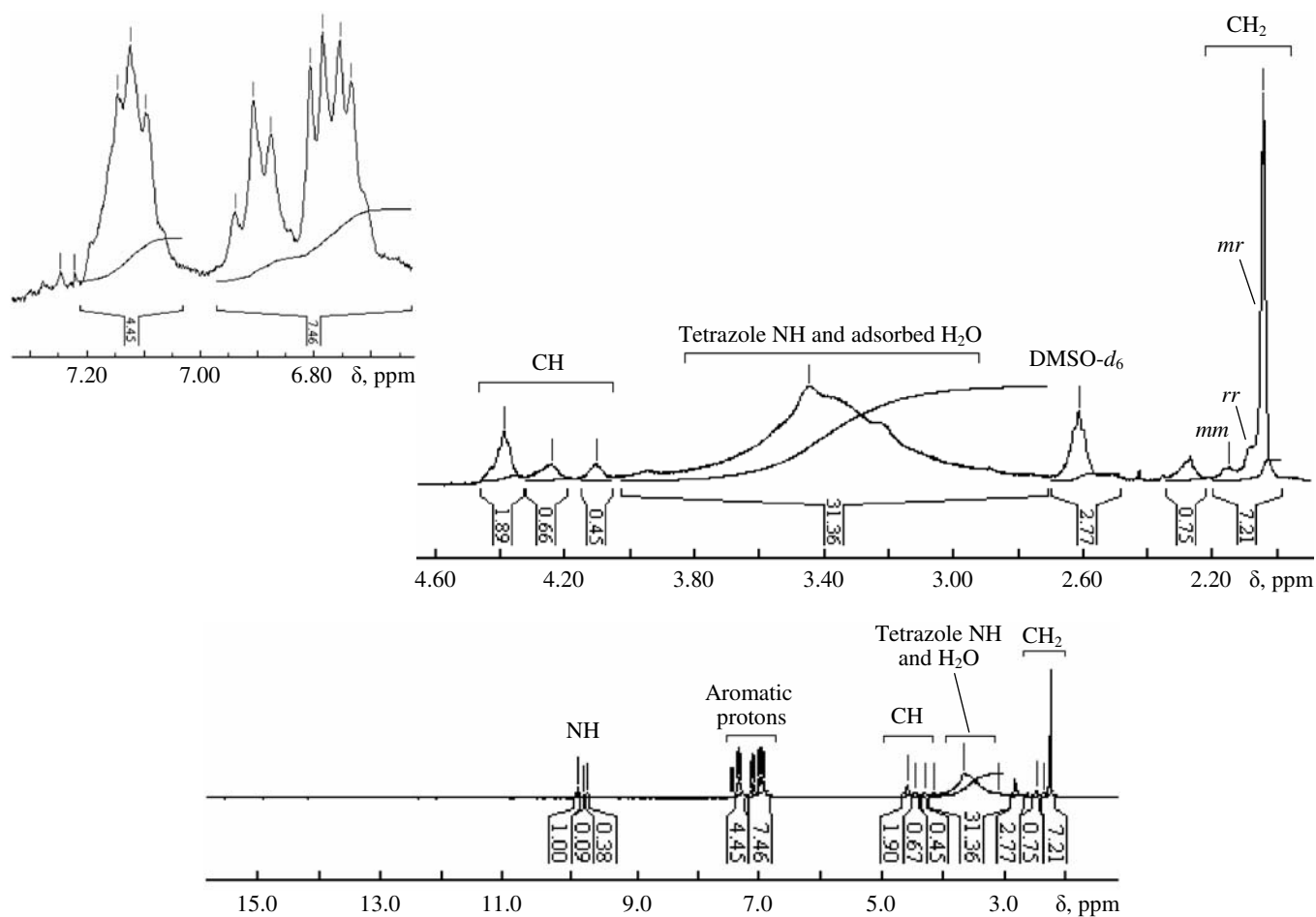


Fig. 3. ^1H NMR spectrum ($\text{DMSO}-d_6$) of homopolymer VII.

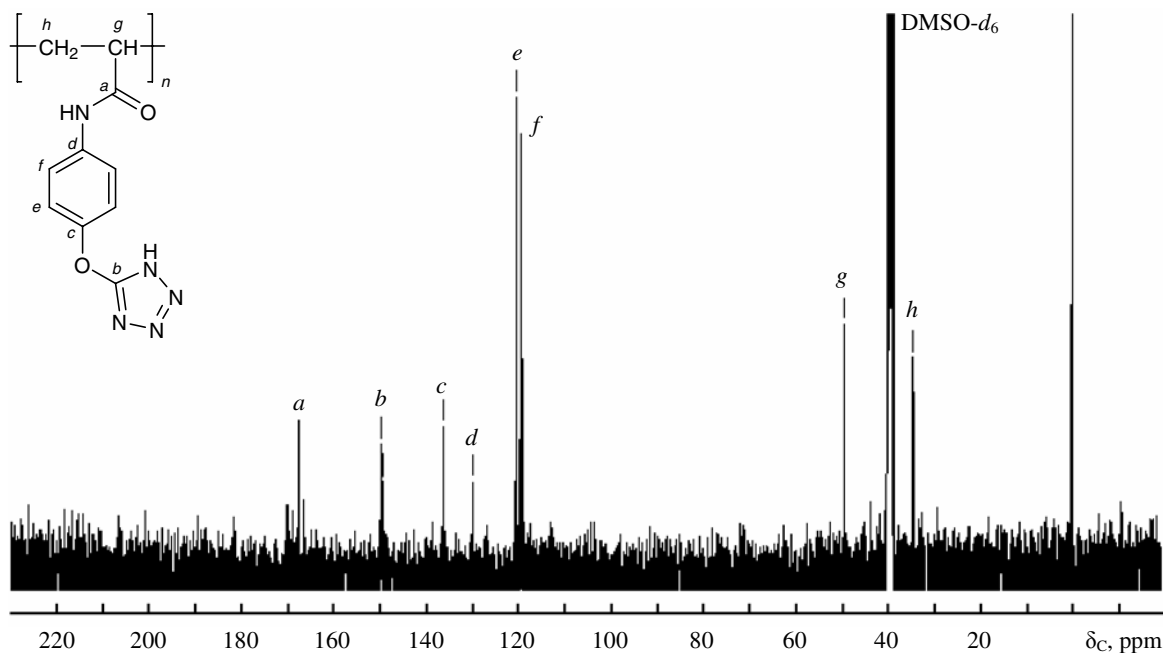
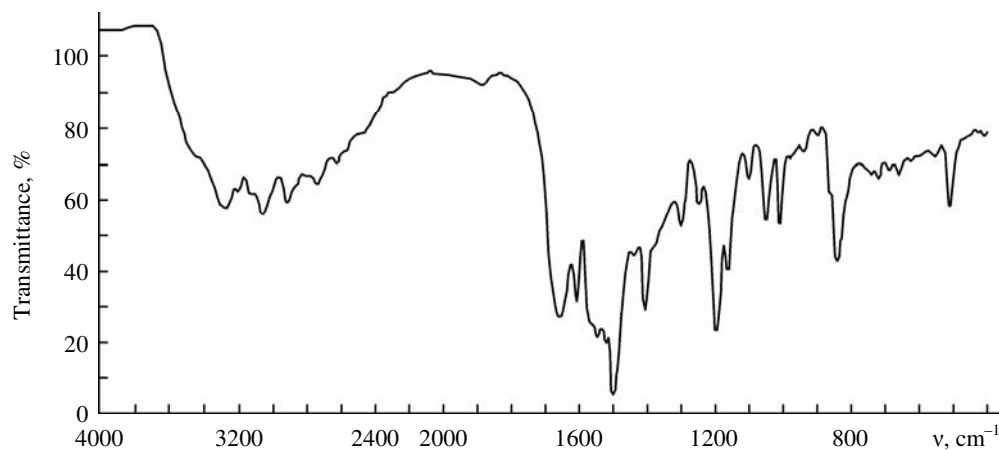
Fig. 4. ^{13}C NMR spectrum ($\text{DMSO}-d_6$) of homopolymer VII.

Fig. 5. FT-IR spectrum (KBr) of homopolymer VII.

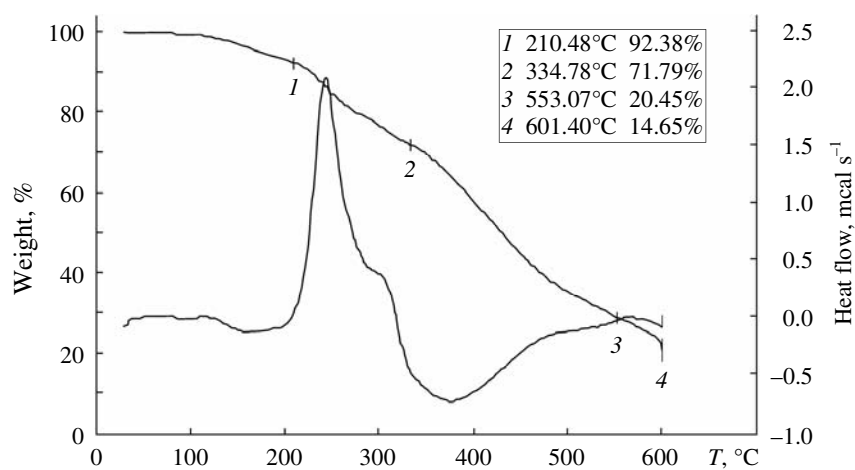
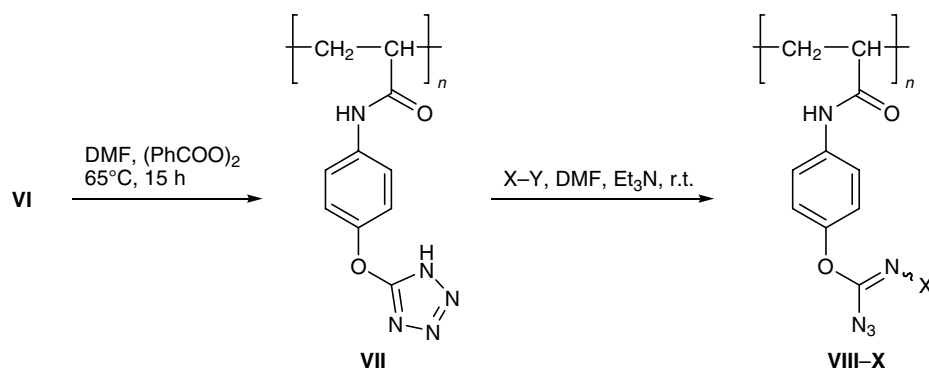


Fig. 6. DSC-TGA thermograms of homopolymer VII.

Scheme 3.



VIII, X = CN, Y = Br; **IX**, X = CF₃SO₂, Y = Cl; **X**, X = *p*-MeC₆H₄SO₂, Y = Cl.

trum of monomer **VI**) and appearance of two new signals at δ_{C} 49.45 and 34.51 ppm (main chain carbon atoms in the homopolymer) provide strong evidences to the formation of polymer. The ¹³C NMR spectrum was recorded with strong amplification (Fig. 4) due to very low concentration of the polymer in solution. Only the predominant atactic sequence (*mr*) is distinguishable in the spectrum, while the other sequences are hidden within the baseline noise.

The high intrinsic viscosity of a solution of homopolymer **VII**, analytical data (C, H, N), and FT-IR spectra provide further support for the polymerization reaction. The elemental composition of **VII** is in a good agreement with the assumed polymer (or monomer) structure, indicating that no decomposition of the monomer occurred during the polymerization. The

absorption band at 1635 cm⁻¹ appearing as a shoulder in the spectrum of **VI** ($\nu_{\text{C}=\text{C}}$, Fig. 1) was not observed in the spectrum of homopolymer **VII** (Fig. 5).

The thermal behavior of homopolymer **VII** was studied by the DSC and TGA techniques (Fig. 6). The thermogram shows that polymer **VII** tends to adsorb water. Weight loss of the polymer can be divided into three main stages. The first stage (110–210.5°C) is characterized by a weight loss of 7.62% and is an endothermic process. It includes removal of physically adsorbed water. In the second stage, two closely located exothermic peaks are distinguished. The first of these corresponds to a weight residue of 71.79 % of the initial weight (210.5–290°C). This step is highly exothermic; it involves decomposition of the tetrazole ring with evolution of gaseous nitrogen. The second

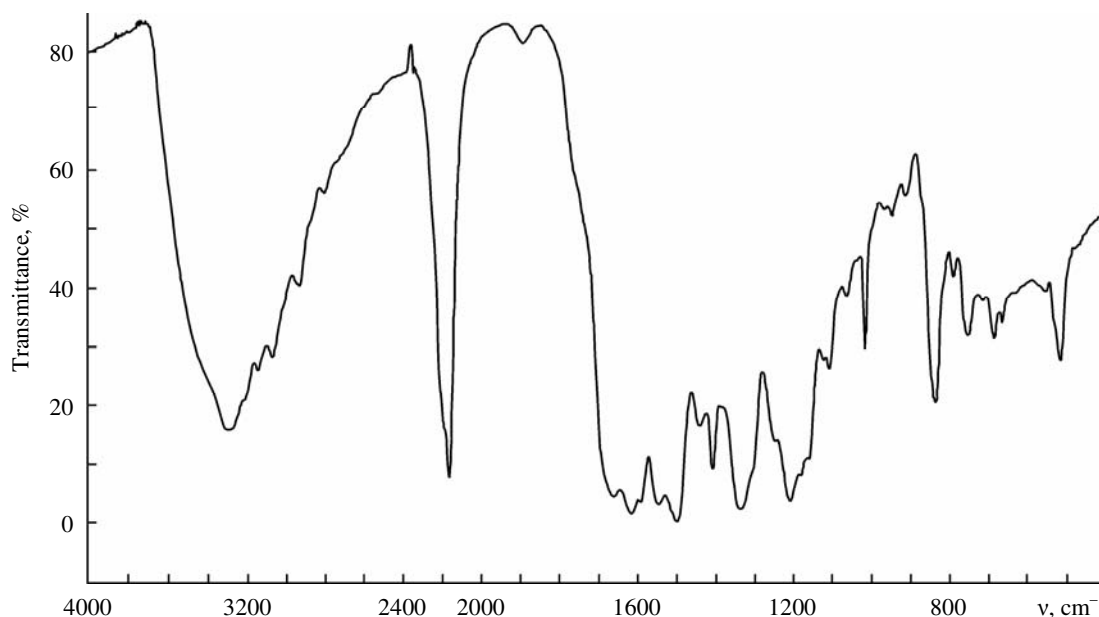


Fig. 7. FT-IR spectrum (KBr) of cyano derivative **VIII**.

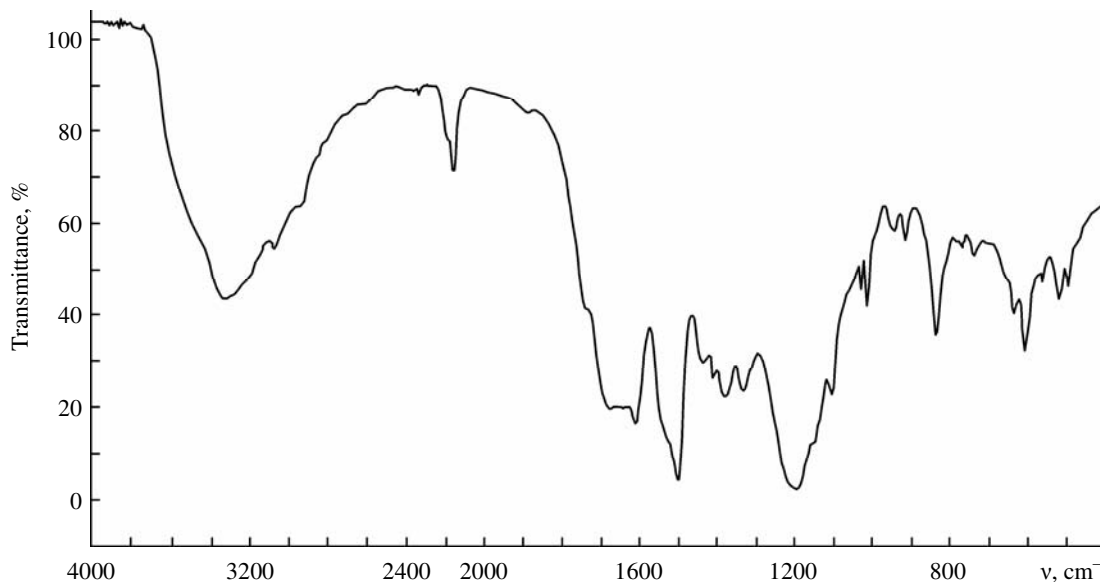


Fig. 8. FT-IR spectrum (KBr) of trifluoromethylsulfonyl derivative **IX**.

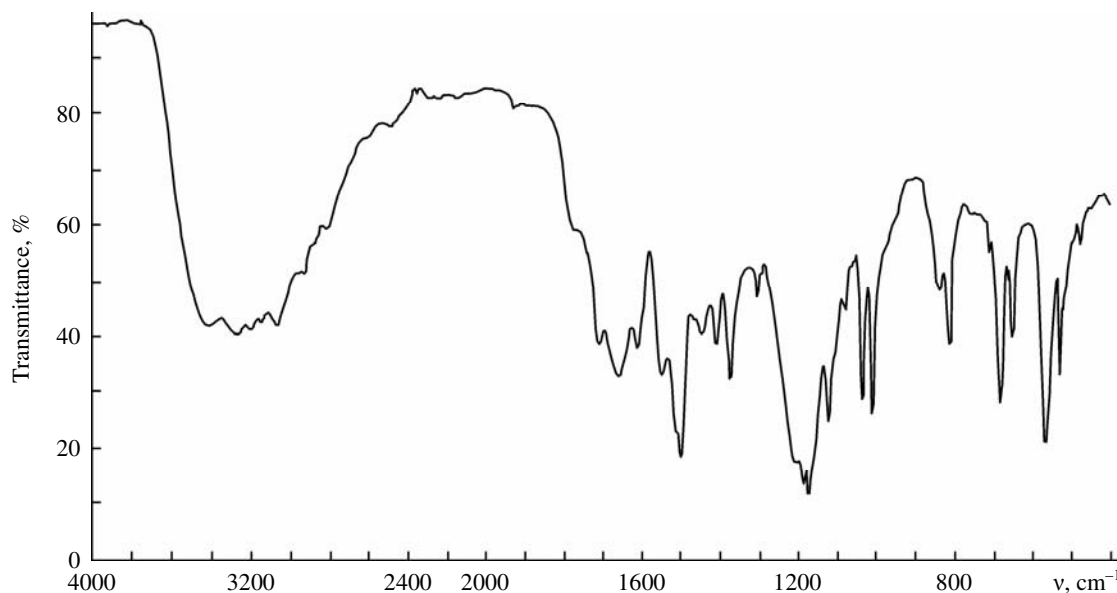


Fig. 9. FT-IR spectrum (KBr) of *p*-tolylsulfonyl derivative **X**.

step gives a small exothermic peak on the DSC curve; it continues until a temperature of 334.8°C is reached and is likely to correspond to decomposition of the remainder of the tetrazole ring. In the final stage, a broad endothermic peak on the DSC curve extends to a temperature of 553.1°C. At that temperature, the weight of the polymer decreases to 28.45% of the initial weight as a result of decomposition of the polymer backbone. The char yield of the polymer is 14.65% at 601.5°C.

Reactions of compounds containing a 1*H*-tetrazole group with *p*-toluenesulfonyl chloride, cyanogen bro-

mide, and trifluoromethanesulfonyl chloride are well known. They lead to the formation of the corresponding imidoyl azide derivatives [23–27]. In this work, we made attempts to prepare imidoyl azide derivatives of homopolymer **VII** according to Scheme 3. The resulting derivatives **VIII–X** were insoluble in common NMR solvents; therefore, only their FT-IR spectra were recorded in KBr. The FT-IR spectrum of cyano derivative **VIII** showed two overlapped strong absorption bands at 2200 and 2166 cm⁻¹ (Fig. 7). This spectrum could not confirm the formation of imidoyl azide derivative, for the azide band is obscured by the cyano

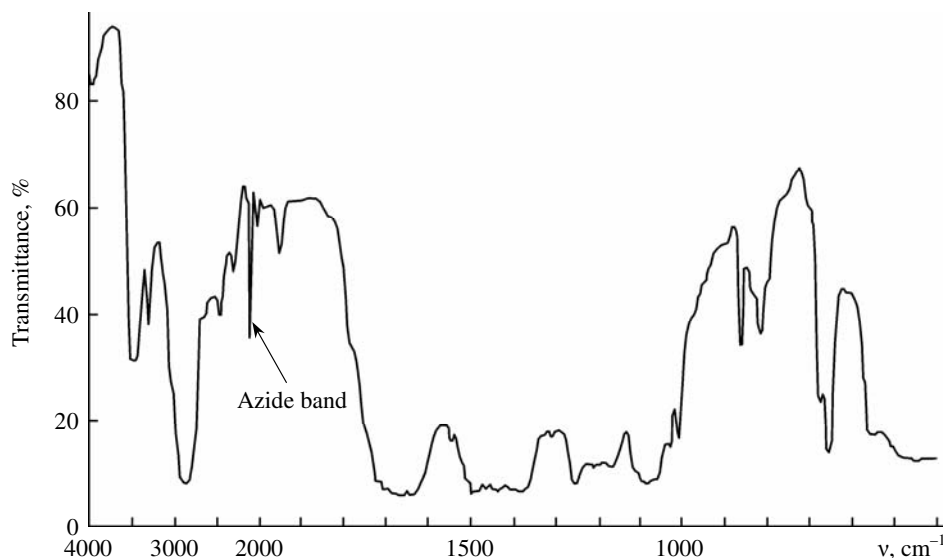


Fig. 10. FT-IR spectrum (DMF) of the crude reaction mixture obtained from homopolymer **VII** and *p*-toluenesulfonyl chloride, recorded in 2 h after the the reaction started.

group absorption. On the other hand, the spectrum indicates addition of cyano group to the 1*H*-tetrazole ring. In the FT-IR spectrum of trifluoromethylsulfonyl derivative **IX** we observed no NH absorption, while two overlapped bands with weak and medium intensity were present at 2200 and 2163 cm^{-1} , respectively (Fig. 8). These absorption bands indicate the formation of imidoyl azide derivative.

No azide band was observed in the FT-IR spectrum of tosyl derivative **X** (Fig. 9), but the spectrum of the reaction mixture obtained from homopolymer **VII** and *p*-toluenesulfonyl chloride in DMF, recorded in 2 h after the reaction started, clearly showed an azide band (Fig. 10) which disappeared when the reaction was complete. Presumably, imidoyl azide derivative **X** undergoes decomposition during workup. Azides are known to be relatively unstable compounds.

Thus we have synthesized monomeric *N*-[4-(1*H*-tetrazol-5-yloxy)phenyl]acrylamide (**VI**) and the corresponding homopolymer **VII** by radical initiation. Their structures were characterized by common techniques. The conversion of the tetrazole ring in the homopolymer to imidoyl azide derivatives was also studied. These transformations demonstrate that 5-aryloxy-1*H*-tetrazole residues can be converted into other functional groups in a polymeric system.

EXPERIMENTAL

The ^1H and ^{13}C NMR, FT-IR, and mass spectra (direct injection) and elemental analyses were obtained at the Justus Liebig University of Giessen (Germany).

The melting points were determined on a Gallenkamp melting point apparatus. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed at the Polymer and Petrochemical Research Center of Iran. All starting compounds and solvents were purified before use according to standard techniques. 4-(1*H*-Tetrazol-5-yloxy)aniline (**V**) was prepared by hydrolysis of *N*-[4-(1*H*-tetrazol-5-yloxy)-phenyl]acetamide as described in [26].

***N*-[4-(1*H*-Tetrazol-5-yloxy)phenyl]acrylamide (VI).** A solution of 0.5 ml (6.15 mmol) of acryloyl chloride in 5 ml of benzene (preliminarily dried over metallic sodium) was added dropwise under stirring to a suspension of 2.18 g (12.31 mmol) of 4-(1*H*-tetrazol-5-yloxy)aniline (**V**) in 15 ml of anhydrous benzene. The mixture was stirred overnight, and the precipitate was filtered off and dried under reduced pressure until constant weight. To remove excess amine **V**, the crude product was treated with 100 ml of 10% hydrochloric acid, the mixture was stirred for 2 h at room temperature, and the precipitate was filtered off, washed with water, and dried under reduced pressure. Yield 68.6%, mp 127–128°C. The FT-IR spectrum is shown in Fig. 1). ^1H NMR spectrum (400 MHz, $\text{DMSO-}d_6$), δ , ppm: 10.27 s (1H), 7.75 d (2H, $J = 9$ Hz), 7.31 d (2H, $J = 9$ Hz), 6.45 d.d (2H, $J = 17, 10$ Hz), 6.29 d.d (2H, $J = 18, 2$ Hz); 5.79 d.d (2H, $J = 10, 2$ Hz), 12.00–15.40 br (1H) (a very broad signal in the spectrum recorded at 90 MHz). ^{13}C NMR spectrum (100 MHz, $\text{DMSO-}d_6$), δ_{C} , ppm (Fig. 2): 166.46, 163.04, 149.66, 136.13, 131.65, 126.67, 120.63, 119.25. Mass spectrum: m/z 231 (I_{rel} 20.30%) [M] $^+$.

Poly{1-[4-(1H-tetrazol-5-yloxy)phenylcarbamoyl]ethylene} (VII). A solution of 2.00 g (8.66 mmol) of monomer **VI** and 0.040 g (1.65 mmol) of benzoyl peroxide in 1.5 ml of DMF was prepared, and dry oxygen-free nitrogen (purity 99.999%) was slowly bubbled through the solution for 15 min to remove dissolved oxygen. The reaction vessel was sealed and immersed into an oil bath, and the mixture was stirred for 15 h at 85°C. The resulting reddish solution was poured into 50 ml of chloroform under vigorous stirring. The precipitate was separated by centrifugation and dried under reduced pressure for 10 h at 120°C to obtain 0.48 g (24%) of brown polymer **VII**, $\eta_{\text{int}} = 1.47$ g dl (0.0500 g, 10 ml of DMF, 24°C). ^1H NMR spectrum (400 MHz, DMSO- d_6), δ , ppm (Fig. 3, *a-c*): 9.77–9.61 m (1H), 7.83–6.83 m (5H), 4.39–4.10 m (1H), 3.94–2.89 br, 2.10–2.03 m (2H). ^{13}C NMR spectrum (50 MHz, DMSO- d_6), δ_{C} , ppm (Fig. 4): 167.60, 149.61, 136.19, 129.89, 119.81, 119.35, 49.45, 34.51. The FT-IR spectrum is shown in Fig. 5. Found, %: C 49.86; H 4.18; N 29.08. $\text{C}_{10}\text{H}_9\text{N}_5\text{O}_2$. Calculated (including 4.19% of water), %: C 50.35; H 4.13; N 28.66.

Poly(1-{4-[azido(cyanoimino)methoxy]phenylcarbamoyl}ethylene) (VIII). A 10-ml round-bottom flask equipped with a mechanical stirrer was charged with a solution of 0.200 g (0.87 mmol) of homopolymer **VII** and 0.37 g (3.46 mmol) of cyanogen bromide in 3 ml of DMF. The solution was cooled to 0°C, and 0.5 ml (3.46 mmol) of triethylamine was added dropwise. Triethylamine hydrobromide separated from the solution during the process. The mixture was stirred for 24 h at room temperature, poured into 30 ml of distilled water, and stirred for 15 min, and the precipitate was separated by centrifugation and dried under reduced pressure at 40°C. The product was a pale brown powder insoluble in common organic solvents; it did not melt below 350°C [24]. The IR spectrum is shown in Fig. 7.

Poly(1-{4-[azido(trifluoromethylsulfonylimino)methoxy]phenylcarbamoyl}ethylene) (IX) was obtained in a similar way. Pale brown powder, insoluble in common organic solvent; the product did not melt below 350°C. The IR spectrum is shown in Fig. 8.

Poly(1-{4-[azido(*p*-tolylsulfonylimino)methoxy]phenylcarbamoyl}ethylene) (X) was obtained in a similar way. The product did not melt below 350°C and was insoluble in common organic solvents. The IR spectrum is shown in Fig. 9.

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ysis and recording the NMR, FT-IR, and mass spectra. The authors also thank Isfahan University of Technology for financial support.

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