New Polyelectrolytes Based on 4-Vinyl-1,2,3-triazole and 1-Vinylimidazole

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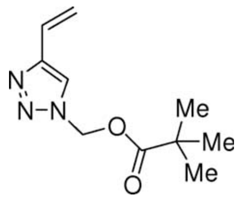
ABSTRACT: Copolymers of 4-vinyl-1,2,3-triazole and 1-vinylimidazole (VI) were obtained by radical copolymerization of (4-vinyl-1H-1,2,3-triazol-1-yl)methyl pivalate with VI followed by alkali hydrolysis. Reactivity ratios of the triazole and imidazole monomers are 0.51 and 0.30, respectively. Theoretical quantum-chemical calculations by the PM3 semiempirical method give close values, which show that the obtained reactivity ratios reflect the activity of the vinyl groups. Polyelectrolyte properties of the copolymers were studied by potentiometric titration. Hydrogen bonds between the protonated triazole cycle and the triazole or imidazole units were found to considerably influence the solubility and solution properties of the copolymers. © 2012 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 50: 1539–1546, 2012

KEYWORDS: light scattering; quantum chemistry; radical polymerization; vinylimidazole; vinyl triazole

INTRODUCTION Azole-containing vinyl polymers have been studied since the 1960s. Among such polymers, the most investigated polymers to date have been the derivatives of vinylimidazoles (see ref. [1] and references mentioned in it) and vinyltetrazoles.[2] The attention gained by polymers of 1-vinylimidazole (VI) is understandable, especially because of the ready commercial availability of the monomer. Tetrazole-containing polymers were found to be attractive mainly as components of solid rocket propellants and explosives. Some hydrophilic poly(vinylazoles) were later studied as potential biologically active substances.[2–4] Crosslinked polymers are effective sorbents of metal cations due to the electron-donor properties of pyridinic nitrogen atoms in the azole cycles. Polymers of N-unsubstituted C-vinylazoles contain basic nitrogen atoms as well as an acidic N-H group in one heterocycle. This combination explains some unusual properties of these polymers, such as the low water solubility of poly(5-vinyltetrazole), despite the high hydrophilicity of the corresponding monomer[5] and high proton mobility in films containing N-H imidazole or triazole moieties.[6–10] Polymers of C-vinyltriazoles have been the least studied group of such compounds because of difficulties in synthesizing the monomers. 4-Vinyl-1,2,3-triazole (VT) was obtained by a multistage procedure,[11] and until recently, this method was the sole available for C-vinyltriazole. Poly(4-vinyl-1,2,3-triazole) (PVT) is a promising polymer for the design of proton-conducting membranes; its conductivity is 100 times higher than that of the imidazole-containing polymer.[7,8] The development of "click chemistry" methods has resulted in the facilitation of the synthesis of VT and its derivatives.[12–14]

This work is devoted to the copolymerization of VT with VI and to the study of the acid-base properties of the copolymers in comparison with their homopolymers. VI is a weak base and was used in the synthesis of carboxylic polyampholytes with a precisely adjustable isoelectric point (IEP) between 2.8 and 6.7.[15] The triazole cycle is a weaker acid compared to the carboxylic group, so we expect that the IEP range of imidazole-containing polyampholytes can be expanded up to the alkali area. VT has been introduced in copolymerization in a protected form as (4-vinyl-1H-1,2,3-triazol-1-yl)methyl pivalate (VTp), which is the precursor of VT:



This substance is preferable to unprotected 4-vinyl-1H-1,2,3-triazole for two reasons: absence of acid-base interactions with VI, which can complicate copolymerization mechanisms, and the easy and quantitative removal of the protective group from the final polymer. It is interesting to note that the abovementioned protection group is not easy to remove from the monomer.[14]

Additional Supporting Information may be found in the online version of this article.

EXPERIMENTAL

Materials

Ethanol, diethyl ether, hexane, sodium hydroxide (NaOH), and 0.1 M and 1 M solutions of NaOH and HCl were purchased from Sigma Aldrich, Fisher, or Acros Chemicals and used without further treatment. VI (Sigma Aldrich) was purified from stabilizers by vacuum distillation before use. 2,2′-Azobis(isobutyronitrile) (AIBN, Sigma Aldrich) was crystallized from ethanol.

VTp was synthesized according to the procedure[12] starting from 3-butyn-1-ol with some minor modifications. To a solution of 3-butyn-1-ol (10.0 g, 142.6 mmol) and triethylamine (43.4 g, 428 mmol) in dichloromethane (900 mL) at 0 °C was added methanesulfonyl chloride (21.2 g, 184.6 mmol) dropwise over 1 h under nitrogen. The reaction mixture was allowed to warm up to ambient temperature and was stirred under nitrogen for 16 h at ambient temperature. On completion, the reaction mixture was washed with 1 M HCl (2×300 mL) and with Brine (1×300 mL). The organic extract was dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue after evaporation was subjected to column chromatography eluting with dichloromethane to obtain but-3-yn-1-yl methanesulfonate (15.9 g, 75%) as an yellow liquid(ES+) *m/z* 149.04 (M+1). The compound was used in the next step without further characterization.

A 500-mL flask equipped with magnetic stir bar was charged with azidomethyl pivalate[16] (6.83 g, 40.6 mmol), but-3-yn-1-yl methanesulfonate (6.10 g, 40.6 mmol), and 60 mL of *t*-butanol. In a separate flask, sodium ascorbate (2.40 g, 12.14 mmol) and $CuSO_4$ (0.324 g, 2.02 mmol) were introduced to 60 mL of deionized water. The aqueous mixture was then added in one portion to the *t*-butanol mixture in the first flask. The reaction mixture was vigorously stirred under nitrogen at ambient temperature for 16 h. On completion, the reaction mixture was concentrated under reduced pressure and then extracted with dichloromethane (3×60 mL). The organic fractions were combined, dried over $MgSO_4$, and filtered, and the filtrate was concentrated under reduced pressure. The residue after evaporation was subjected to column chromatography eluting with ethyl acetate–hexanes mixture (1:1) to obtain (4-(2-((methylsulfonyl)oxy)ethyl)-1H-1,2,3-triazol-1-yl)methyl pivalate (9.17 g, 74%) as a white solid. (ES+) *m/z* 306.36 (M+1). The compound was used in the next step without further characterization.

A 250-mL round-bottom flask equipped with magnetic stir bar was charged with (4-(2-((methylsulfonyl)oxy)ethyl)-1H-1,2,3-triazol-1-yl)methyl pivalate (4.43 g, 14.5 mmol) and 1,2-dimethoxyethane (145.0 mL). To this solution, NaI (6.53 g, 43.6 mmol) was added, followed by 1,8-Diazabicyclo[5.4.0]undec-7-ene (DBU) (4.42 g, 29.1 mmol). After addition of all reagents, the reaction mixture was heated to reflux for 30 min. On completion, the reaction mixture was participated between dichloromethane and water (100 mL:100 mL), and the aqueous layer was extracted with dichloromethane (3×100 mL). The organic fractions were combined, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The residue after evaporation was subjected to column chromatography eluting with ethyl acetate–hexanes mixture (1:1) to afford VTp (2.01 g, 66%) as an off-white solid.

^{1}H NMR (300 MHz, $CDCl_3$) δ 7.74 (s, Ar, 1H), 6.67 (dd, J = 28.9, 11.1 Hz, C**H**=CH_2, 1H), 6.63 (s, NC$\mathbf{H}_2$O, 2H), 5.91 (dd, J = 17.7, 1.0 Hz, *cis*-CH=C$\mathbf{H}_2$, 1H), 5.35 (dd, J = 12.4, 1.2 Hz, *trans*-CH=C$\mathbf{H}_2$, 1H), 3.68(s, CO(C$\mathbf{H}_3$)$_3$, 9H), (ES+) *m/z* 210.26 (M+1).

Synthesis of Copolymers

PVTp and VTp–VI copolymers were synthesized by radical polymerization in ethanol (8 mL of 25% solution) under the action of AIBN (1% from the monomer mass) at 60 °C under an argon atmosphere in hermetically sealed 30-mL vials. The resulting solutions in the case of PVTp were precipitated into diethyl ether–hexane (2:1) or, in the case of copolymers, into diethyl ether. The solution–precipitant ratio was 1:10. The products were then reprecipitated from ethanol, washed with the precipitant, and dried in vacuum. The composition of the monomer mixtures, duration of the reaction, and yield are summarized in Table 1.

The obtained polymers were used for the synthesis of PVT and VT–VI copolymers by alkali hydrolysis as outlined below:

PVTp (1 g, 4.79 mmol) was added to 1 M NaOH solution (10 mL, 10 mmol NaOH) and ethanol (5 mL). The mixture was heated at 40 °C for 2 h with continual stirring, purified by dialysis against water through a cellophane membrane (8 kDa cutoff), and freeze dried. The yield was 0.385 g (86%). VTp–VI copolymers were hydrolyzed using a similar procedure, by decreasing the amount of alkali in proportion to the VTp content in the copolymer.

Characterization

^{1}H and ^{13}C NMR spectra were recorded on a Bruker AVANCE 400 spectrometer in D_2O. Typical spectra of the polymers and their assignment can be found in the Supporting Information. Infrared spectra were recorded on an Infralum FT-801 spectrophotometer (SIMEX, Russia). Potentiometry measurements were performed on a “Multitest” ionometer using a combined pH electrode in a temperature-controlled cell at 20 ± 0.02 °C under an argon atmosphere. The pH of the solutions was adjusted up to 11.5 using 0.1 M NaOH; 0.1 M HCl was used as a titrant. The concentration of the copolymers was 1.5 mg/mL.

Dynamic light scattering (DLS) experiments were performed using a LAD-079 instrument built at The Institute of Thermophysics (Novosibirsk, Russia). All solutions were purified of dust using filter units with 0.45 μm pore size (Sartorius 16555-Q Minisart syringe filters). The experiments were performed at 20 ± 0.02 °C. Measurements were performed using a 650-nm solid-state laser at 36°, 54°, 72°, and 90° scattering angles. Correlation functions were analyzed with a polymodal model using a random-centroid optimization method.[17] Results obtained at 90° are presented in this article; the data at other angles were analogous. Viscosity measurements were performed in a capillary viscometer at 20 ± 0.02 °C.

TABLE 1 Copolymerization of VTp with VI

Run	VTp in Initial Mixture (mol %)	Time (h)	Yield (%)	VTp in Copolymer (mol %)	[η][a] (dL/g)	Rh[b] (nm) [Intensity (%)]	pK_o (VT units)	Turbidity Interval (pH)
1	100	19	62	100	0.58	88 (47), 670 (53)	9.8	2.5–9.2
2	100	45	100	100	0.55	–	9.8	2.5–9.2
3	88.7	26	88	86.5	0.54	54 (35), 1,100 (65)	9.6	1.5–9
4	70.0	26	84	67.4	0.52	38 (41), 360 (59)	9.5	1.5–9
5	50.3	26	71	52.4	0.49	14 (6), 270 (94)	9.2	1.5–9
6	30.2	26	69	37.2	0.54	52 (27), 340 (73)	9.3	6–9
7	9.5	26	53	15.2	0.43	66 (77), 600 (23)	8.9	6.6–9
8	89.7	6	51.1	81.8	–	–	–	–
9	70.1	6	50.6	64.0	–	–	–	–
10	48.8	6	18.5	58.2	–	–	–	–
11	29.1	6	26.0	46.9	–	–	–	–
12	9.4	6	12.5	20.3	–	–	–	–
13	0	6	3.6	0	0.23	71		

[a] in 0.1 M NaOH + 1 M KBr.

[b] in 0.1 M HCl + 0.1 M NaCl.

Quantum-chemical calculations were performed with the HyperChem program.[18]

RESULTS AND DISCUSSION

Synthesis of Copolymers

VTp is easily polymerizable under the action of AIBN. Yields of the copolymers decrease with an increase in the VI content in the initial monomer mixture (Table 1); the yield reduced to 53 at 9.5% VTp. The compositions of the copolymers are calculated from NMR data. Yields of copolymers 3–7 (Table 1) were unduly high for the calculation of reactivity ratios, so we obtained samples at less than 50% yields. Reactivity ratios of the monomers were calculated by the integral method described by Kuo and Chen,[19] which was modified according to[20] to obtain an equation symmetrically relative to r_1 and r_2:[21]

$$1\Big/\sqrt{kx} - \sqrt{kx} = \sqrt{k/x}r_2 - \sqrt{x/k}r_1,$$

where $k = \frac{m_{20}M_1}{m_{10}M_2}$; $x = \frac{m_1}{m_2}$; and m_{i0}, m_i, and M_i are the monomer fractions in the initial monomer mixture, monomer mixture after reaction, and copolymer, respectively.

The following values are obtained: $r_{\rm VTp} = 0.51 \pm 0.03$ and $r_{\rm VI} = 0.30 \pm 0.02$. These reactivity ratios are typical for systems having an azeotropic point that corresponds to 59.3 mol % VTp, and experimental data confirm these values (Fig. 1).

Reactivity ratios calculated according to the classical Mayo-Lewis equation[22] are often effective values because in addition to the activity of vinyl groups, they depend on many other factors: specific interactions between functional groups of monomers, preferential adsorption of a monomer by a macromolecular coil, the effect of the penultimate unit, and so on. One way to verify the correlation between the activities of the monomers with the electronic effect of substituents on the vinyl group is through the quantum chemical simulation of the reactivity ratios. Previously, we have shown[23] that theoretical reactivity ratios can be obtained from activation energies of all elementary stages. These values were calculated as differences between the total energy of the activated complex and the summary energy of the free radical and monomer (see Supporting Information). Reactivity ratios were obtained from the equation $r_i = \exp(-\frac{E_{ii}-E_{ij}}{RT})$, where E_{ii} and E_{ij} are the activation energies of the corresponding elementary reactions. The quantum chemical calculations by the PM3 semiempirical method result in $r_{\rm VTp} = 0.54$ and $r_{\rm VI} = 0.26$; these values are close to the values obtained from the experimental data. Thus, the copolymerization in the VTp–VI system complies with the Mayo-Lewis equation and the obtained reactivity ratios reflect the activity of the vinyl groups.

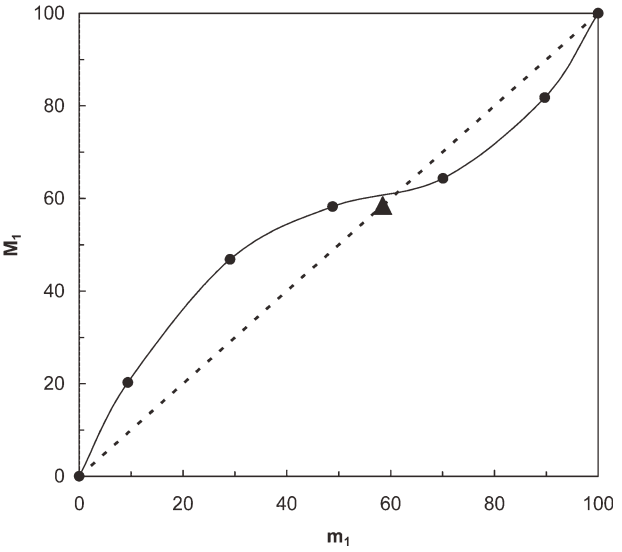


FIGURE 1 Dependence of VTp content in copolymer (M_1, mol %) on VTp in monomer mixture (m_1). Azeotropic point (black triangle) is calculated from reactivity ratios.

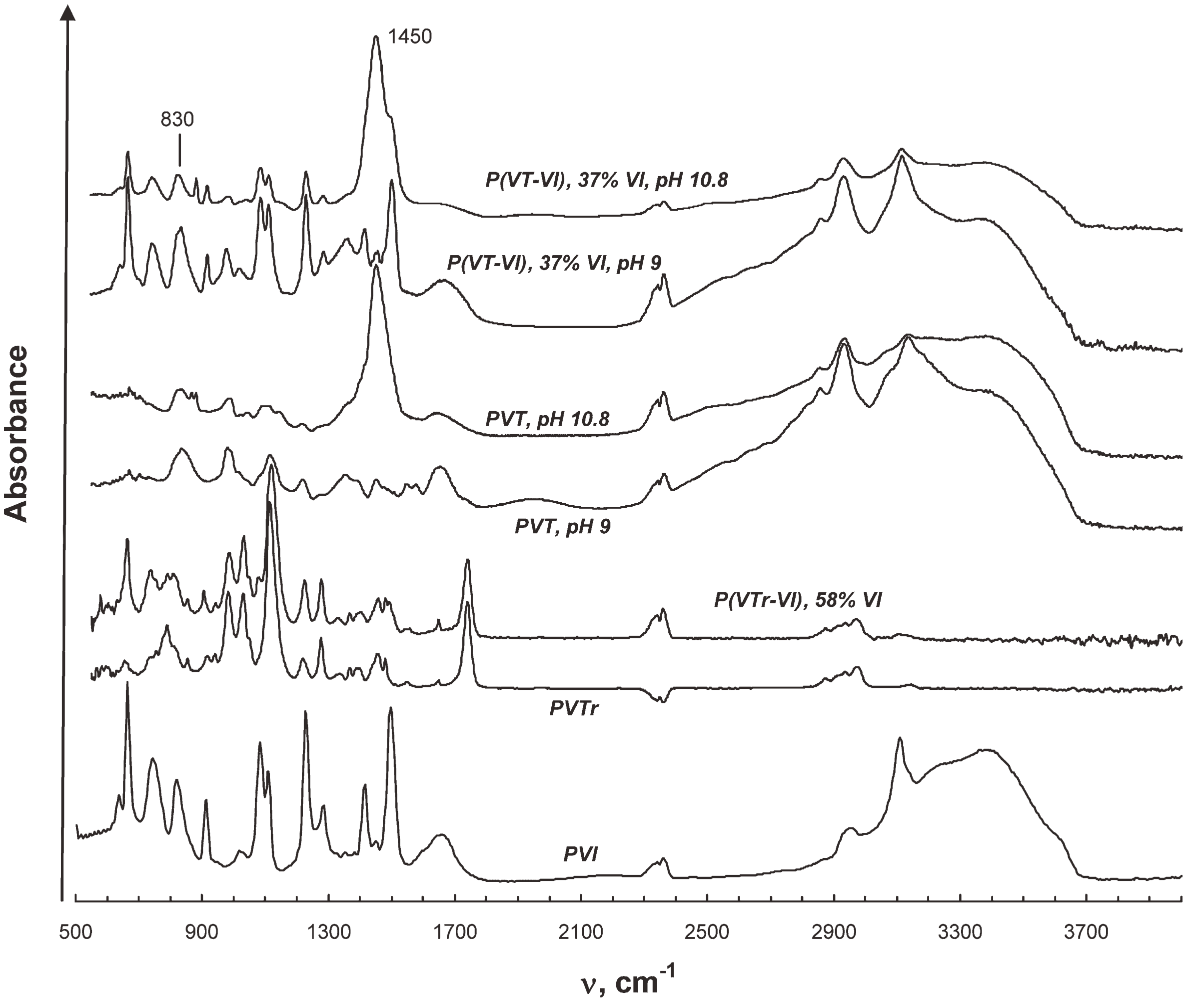


FIGURE 2 IR spectra of (co)polymers.

VTp–VI copolymers were converted into VT–VI copolymers by alkali hydrolysis and purified by dialysis, followed by freeze drying. The reaction can be easily monitored by the disappearance of the C=O band at 1740 cm^{-1} in the IR spectra (Fig. 2), and lines in the ^{13}C NMR spectra at 70 and 177 ppm correspond to $\mathbf{C}H_2$ and $\mathbf{C}(Me)_3$ of the protective group. The obtained copolymers are white solids soluble in water, giving solutions with pH 9–9.5. A decrease in the pH results in the precipitation of the copolymers (Table 1). VT–VI copolymers are soluble in methanol and insoluble in ethanol, dimethylformamide (DMFA), and dimethyl sulfoxide (DMSO), with the exception of a copolymer containing 15.2% VT, which is soluble in both ethanol and DMSO.

The IR spectrum of poly(1-vinylimidazole) (PVI), according to ref. 24, contains bands of stretching vibrations of imidazole cycles (1500, 1415, 1284, and 1228 cm^{-1}), stretching vibrations of azole C—H (1109 and 1083 cm^{-1}), and bending vibrations of the heterocycle (912, 820, 745, 661, and 635 cm^{-1}) (Fig. 2). The main bands in the PVT spectrum are at 1576, 1547, 1450, 1353, 1218, 1113, 980, and 835 cm^{-1}. The band at 1650 cm^{-1} can be assigned to vibrations of water molecules, which are strongly coordinated with NH–triazole cycles, similar to poly(5-vinyltetrazole).[5] The wide band at 2300–3700 cm^{-1} corresponds to associated NH moieties.[5] The spectra of VT–VI copolymers are superpositions of the homopolymers' spectra. It must be mentioned that these spectra are observed for samples obtained from water solutions at pH $<$ 9.5. The isolation of PVT or copolymers by freeze-drying solutions with pH 10–11 results in samples with interesting IR spectra, in which an extremely strong band at 1450 cm^{-1} is observed (Fig. 2). The relative intensity of this band increases with an increase in the content of ionized VT units to more than 0.2–0.3 (Fig. 3), independent of the copolymer composition. Experimental and theoretical studies of IR spectra of triazole and tetrazole anions show that bands near 1450 cm^{-1} are attributed to C—N stretching and C—H deformation vibrations of the cycle.[25] The intensity of this band is low in the case of the 1,2,3-triazole anion[26] but increases drastically for the 1,2,4-triazole cycle. We can suppose that the extreme intensive absorption of PVT and copolymers at 1450 cm^{-1} in samples obtained at pH$>$ 10 is related to the vibrations of the triazole anionic cycle, which are strengthened by some peculiarities of the polymer structure in the solid state. The detailed clarification of this phenomenon is possible by thorough simulation experiments and calculations, which go beyond the scope of this work.

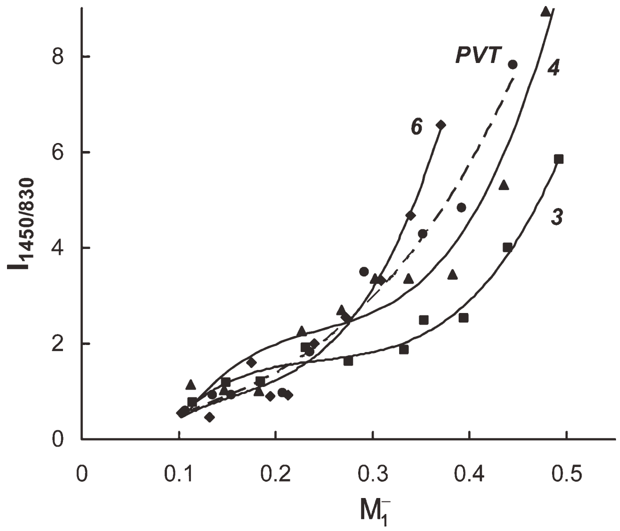


FIGURE 3 Dependence of relative intensity of the bands at 1450–830 cm^{-1} in IR spectra of PVT and copolymers on molar fraction of VT anions in the polymeric chain. Lines labeling corresponds to Table 1.

Properties of the Copolymers in Water Solution

The PVT and VT–VI copolymers are soluble in water under acidic or alkali conditions (Table 1). Study of these solutions with DLS shows the multimodal size distribution of the macromolecules. An increase in the ionic strength did not result in the destruction of the associates, which did not allow us to measure the molecular weight of the copolymers with static light scattering. The solutions of the copolymers and PVT contain particles from two size intervals (Table 1): 14–90 nm, which may be attributed to individual macromolecules, and particles with diameters of more than 500 nm. The presence of the large aggregates is at variance with the filtration of the samples before DLS using 450 nm filters, which is probably related to the reversible destruction of large particles during filtration. Previously, we observed a similar phenomenon in the case of VI–acrylic acid copolymers.[15]

Potentiometry titration curves of PVT and copolymers (Fig. 4) contain a sharp inflection corresponding to the full neutralization of the VT–Na units. Using data on the copolymer composition, we calculated points that corresponded to the presence of VT units in the VT–Na state and points of full VI and VT unit protonation. These neutralization points were used to obtain the ionization degree (α) of the VT units (Fig. 5) and conjugated acids from protonated VT and VI units (Fig. 6). The α values were calculated by taking into account self-ionization and hydrolysis of the acidic units by conventional equations.[27] The p*K* values for the acidic ionization of VT units and for ionization of conjugated acids in the titration area after inflection were obtained using the Henderson–Hasselbalch equation.[28]

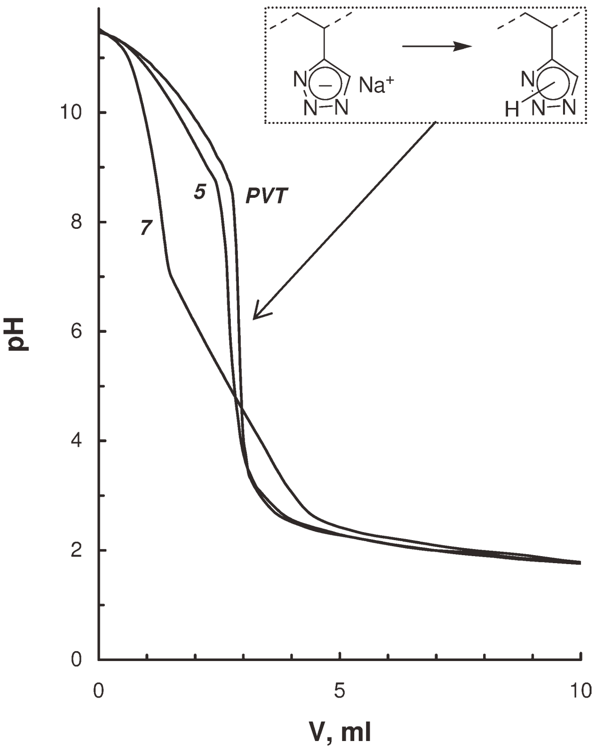


FIGURE 4 Typical titration curves of PVT and copolymers. The inflection corresponds to the neutralization of the VT–Na units according to the scheme. Concentration: 1.5 mg/mL, solution volume: 20 mL, in the presence of 0.1 M NaCl. Titrant: 0.1 M HCl. pH was adjusted up to 11.5 with 0.1 M NaOH before titration. Lines labeling corresponds to Table 1.

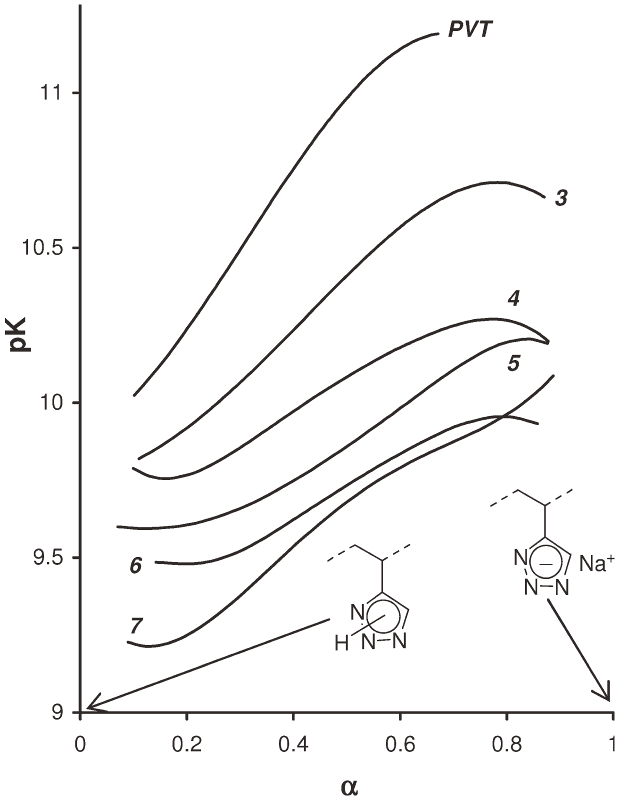


FIGURE 5 Dependence of p*K* of triazole units on ionization degree α. Triazole species corresponded to $\alpha = 0$ and 1 are presented in the figure. Lines labeling corresponds to Table 1.

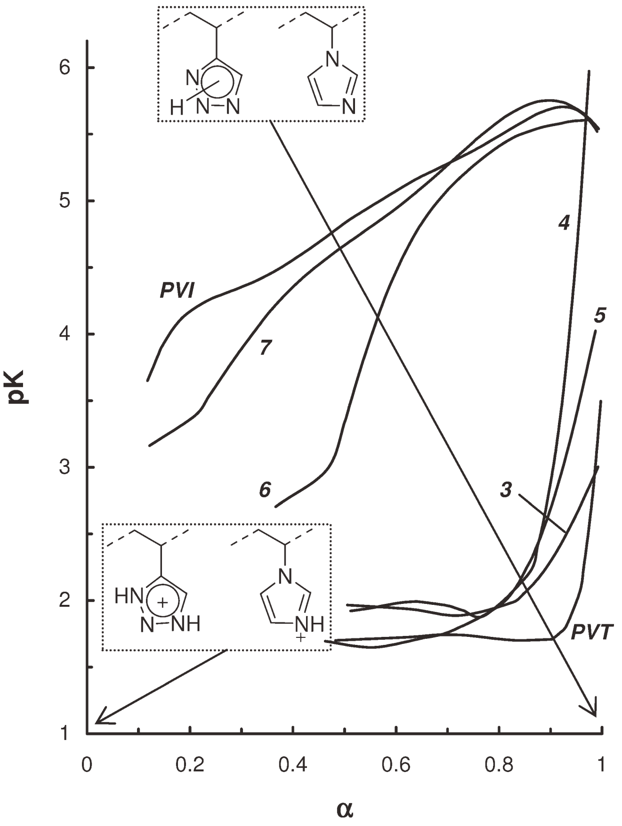
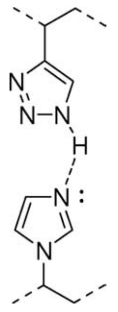


FIGURE 6 Dependence of p*K* on ionization degree α of conjugated acid from VT and VI units. Triazole and imidazole species corresponded to $\alpha = 0$ and 1 are presented in the figure. Lines labeling corresponds to Table 1.

In the case of the acidic ionization of VT units (Fig. 5), we observe an expected increase in p*K* with α, which is related to a decrease in VT acidity owing to the known electrostatic effect. The inclination of the curves decreases with an increase in the VI content in the copolymers, probably because of the dilution of the VT units with nonionized imidazole groups and the corresponding decrease in the electrostatic effect. Copolymer samples 4–7 show a horizontal part at $\alpha < 0.2$–0.3, which is attributed to the destruction of the hydrogen bonds between VT and VI units under neutralization:

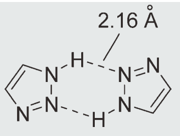
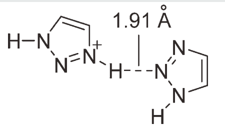
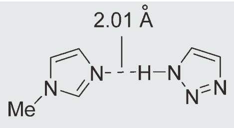
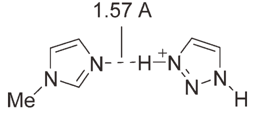


This hydrogen bonding results in the precipitation of PVT and copolymers at pH < 9.2, which corresponds to $\alpha < 0.1$. Characteristic pK_o values were obtained by the extrapolation of the straight parts of the p*K*–α curves to $\alpha = 0$. The obtained data (Table 1) are close to the p*K* of 1,2,3-triazole (9.26)[29] and decrease only slightly with an increase in the VI content. The viscosity of the polymer solutions increases with pH (Fig. 7), and the most pronounced growth is observed up to a content of ionized VT units of 0.2–0.3, which corresponds to the appearance of a 1450 cm^{-1} band in the IR spectra and confirms the assignment of this band to the ionized triazole cycles.

The other titration region is placed in the acidic area and corresponds to the protonation of VT and VI units. The PVI titration curve (Fig. 6) shows an increase in p*K* with α, similar to data published previously,[30] and the characteristic p*K* at $\alpha = 1$ (protonation of the first VI unit) is equal to 5.9. The behavior of PVT and copolymers 3–5 is unusual: relatively high p*K* near $\alpha = 1$, followed by a sharp decrease up to $\alpha = 0.7$–0.9. The extrapolation of p*K* to $\alpha = 1$ for PVT and copolymers is irrelevant owing to their insolubility at $\alpha = 0.9$–1.

The observed high p*K* values for PVT near $\alpha = 1$ are anomalously high, taking into account p*K* = 1.17 for the protonation of 1,2,3-triazole.[29] A similar effect in the case of poly(1-vinyl-1,2,4-triazole)[30] was explained by the involvement of protons in intramolecular donor–acceptor bonds between the polymer units. In the case of PVT, we

TABLE 2 Enthalpy of Hydrogen Bond Formation[a] Between Triazole and Imidazole Units

Structures	Calculated energy of hydrogen bonds (kJ/mol)
 2.16 Å	−53.4
 1.91 Å	−107.0
 2.01 Å	−49.2
 1.57 Å	−133.5

[a] Calculated by *ab initio* Hartree–Fock method using 6-31G** basis set with full geometry optimization. Triazole tautomers with the lowest energy of formation were used.

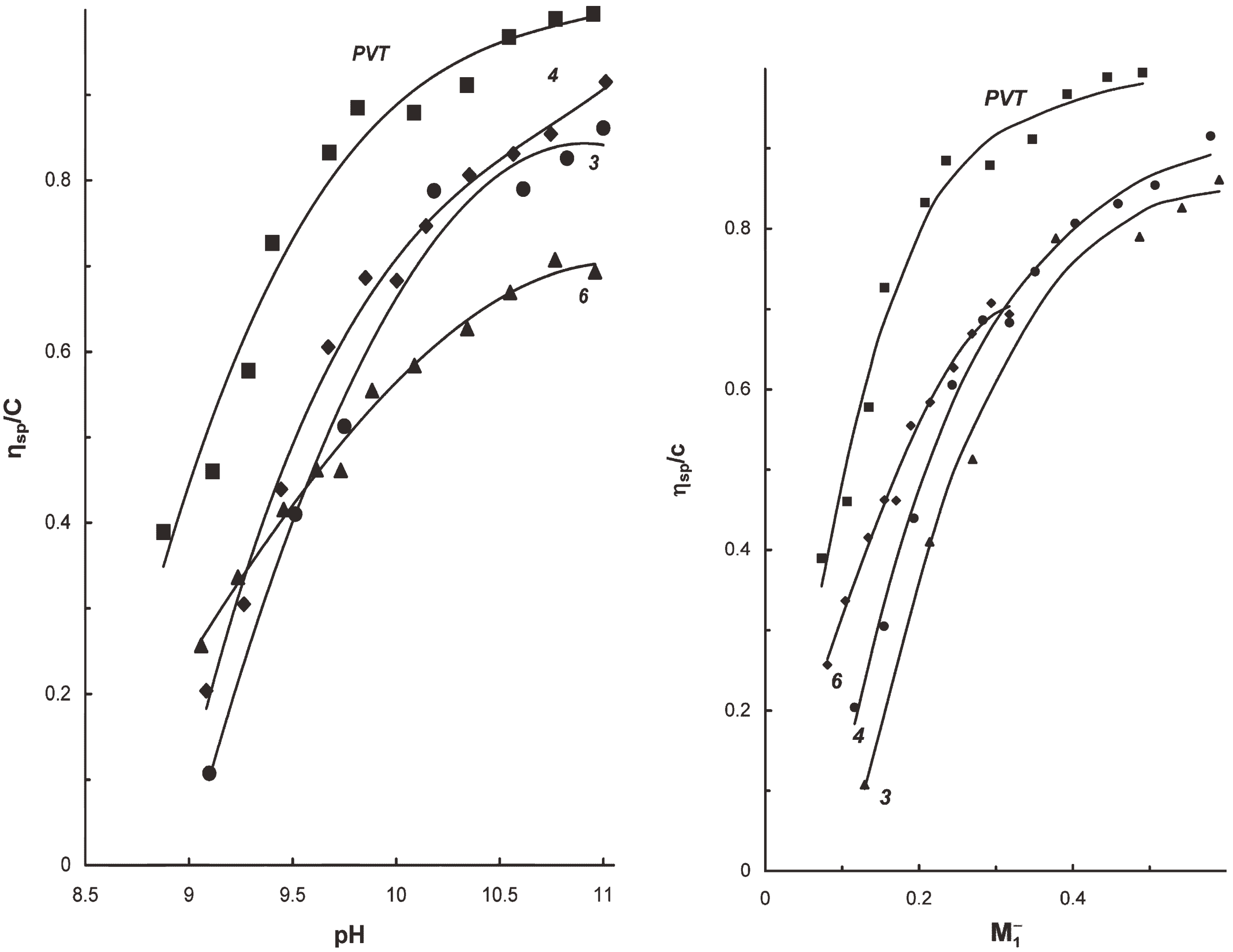


FIGURE 7 Dependence of reduced viscosity on pH and molar fraction of VT anions in the polymeic chain. Lines labeling corresponds to Table 1. Polymer concentration: 1.5 mg/mL, in 0.1 M NaCl.

observe precipitation at pH 9.2 and below; the precipitate dissolves again at pH 2.5, which corresponds to $\alpha = 0.9$ (Fig. 6). We can assume that the insolubility of PVT is a result of hydrogen bonding. Quantum-chemical calculation (Table 2) shows relatively high energy of this bonding, possibly due to the involvement of two hydrogen atoms from both the triazole units. The protonation of one of the azole cycles enhances the bonding drastically: ΔH increases from -53.4 to -107.0 kJ/mol. This strengthening of the hydrogen bonds explains the insolubility of the polymers in acidic media, down to pH 2–2.5. VI units are also able to interact with the N—H bonds of the VT cycles (Table 2), and the protonation of triazole units results in a very stable hydrogen bond ($\Delta H = -133.5$ kJ/mol), whose length (1.57 Å) is lower than the typical value for hydrogen bonds (2 Å). Thus, copolymers containing up to 60% VI units show behavior similar to PVT: high basicity and insolubility at low protonation degrees and solubility after some critical positive charge of the chain, followed by a drop in basicity. Copolymers bearing greater than 60% VI units contain imidazole groups unbounded by triazole cycles and are protonated similar to PVI.

CONCLUSIONS

The compound VTp gives statistical copolymers with VI, and the radical copolymerization of the monomers complies with the Mayo-Lewis equation. The alkali hydrolysis of these copolymers results in VT–VI copolymers. Triazole cycles are capable of acidic dissociation at pH> 9 and protonation in an acidic medium. PVT and copolymers containing greater than 37% VT units are insoluble in water at pH 2–9 owing to hydrogen bonding between acidic N—H of the VT and pyridinic nitrogens in the VT and VI cycles. These polymers show anomalously high basicity of triazole units with protonation up to 10%, which is attributed to triazole cycles that are hydrogen-bonded with other VT or VI units. The ability of PVT to eagerly accept protons probably explains the high proton conductivity of triazole-containing membranes.[8–10] The introduction of imidazole units into the PVT chain increases this effect. Thus, VT–VI copolymers are promising substances for designing membranes to be used for polymer electrolyte membrane fuel cells.

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REFERENCES AND NOTES

1 Annenkov, V. V.; Danilovtseva, E. N.; Saraev, V. V.; Mikhaleva, A. I. *J. Polym. Sci. Part A: Polym. Chem.* **2003,** *41*, 2256–2263.

2 Annenkov, V. V.; Kruglova, V. A. In Polymeric Materials Encyclopedia; Salamone, J. P., Ed.; CRC Press: Boca Raton, **1996; pp 7163–7171.**

3 Sabaa, M. W.; Mohamed, N. A.; Mohamed, R. R.; Khalil, N. M.; Abd El Latif, S. M. *Carbohydr. Polym.* **2010,** *79*, 998–1005.

4 Danilovtseva, E. N.; Annenkov, V. V.; Shmeleva, E. A.; Serd'uk, L. V.; Leshuk, S. I. In Proceedings of the IASTED International Conference on Nanotechnology and Applications, Crete, Greece, Sept 29–Oct 1, 2008; Nicolini, C., Ed.; ACTA Press: Anaheim, Calgary, Zurich, **2008.**

5 Kruglova, V. A.; Kizhnyaev, V. N.; Ivanova, N. A.; Vereshchagin, L. I. *Vysokomol. Soedin. Ser. B* **1987,** *29*, 416–419.

6 Bozkurt, A.; Karadedeli, B. *React. Funct. Polym.* **2007,** *67*, 348–354.

7 Zhou, Z.; Li, S.; Zhang, Y.; Liu, M.; Li, W. *J. Am. Chem. Soc.* **2005,** *127*, 10824–10825.

8 Zhou, Z.; Liu, R.; Wang, J.; Li, S.; Liu, M.; Brédas, J.-L. *J. Phys. Chem. A* **2006,** *110*, 2322–2324.

9 Martwiset, S.; Yavuzcetin, O.; Thorn, M.; Versek, C.; Tuominen, M.; Coughlin, E. B. *J. Polym. Sci. Part A: Polym. Chem.* **2009,** *47*, 188–196.

10 Sanghi, S.; Tuominen, M.; Coughlin, E. B. *Solid State Ionics* **2010,** *181*, 1183–1188.

11 Wouters, G.; Smets, G. *Makromol. Chem.* **1982,** *183*, 1861–1868.

12 Thibault, R. J.; Takizawa, K.; Lowenheilm, P.; Helms, B.; Mynar, J. L.; Fréchet, J. M. J.; Hawker, C. J. *J. Am. Chem. Soc.* **2006,** *128*, 12084–12085.

13 Lundberg, P.; Hawker, C. J.; Hult, A.; Malkoch, M. *Macromol. Rapid Commun.* **2008,** *29*, 998–1015.

14 Takizawa, K.; Nulwala, H.; Thibault, R. J.; Lowenhielm, P.; Yoshinaga, K.; Wooley, K. L.; Hawker, C. J. *J. Polym. Sci. Part A: Polym. Chem.* **2008,** *46*, 2897–2912.

15 Annenkov, V. V.; Danilovtseva, E. N.; Tenhu, H.; Aseyev, V.; Hirvonen, S.-P.; Mikhaleva, A. I. *Eur. Polym. J.* **2004,** *40*, 1027–1032.

16 Loren, J. C.; Krasiński, A.; Fokin, V. V.; Sharpless, K. B. *Synlett* **2005,** *18*, 2847–2850.

17 Box, M. J. *Comput. J.* **1965,** *8*, 42–52.

18 HyperChem^{TM} Professional 8.08, Hypercube, Inc., 1115 NW 4th Street, Gainesville, Florida 32601, USA. According to recommendation of the program developers: http://www.computationalchemistry.com/support/KB/HC75/default.htm#Citation

19 Kuo, J. F.; Chen, C. J. *J. Appl. Polym. Sci.* **1981,** *26*, 1117–1119.

20 Ezrielev, A. N.; Brokhina, E. L.; Roskin, E. S. *Vysokomol. Soedin. Ser. A* **1969,** *11*, 1670–1684.

21 Annenkov, V. V.; Lebedeva, O. V.; Danilovtseva, E. N.; Mikhaleva, A. I. *Polym. Sci. Ser. B* **2001,** *43*, 247–250.

22 Mayo, F. R.; Lewis, F. M. *J. Am. Chem. Soc.* **1944,** *66*, 1594–1601.

23 Annenkov, V. V.; Danilovtseva, E. N.; Smirnov, V. I.; Maksimova, M. A. *Polym. Sci. Ser. B* **2005,** *47*, 201–205.

24 Lippert, J. L.; Robertson, J. A.; Havens, J. R.; Tan, J. S. *Macromolecules* **1985,** *18*, 63–67.

25 Elazhary, A. A.; Suter, H. U.; Kubelka, J. *J. Phys. Chem. A* **1998,** *102*, 620–629.

26 Törnkvist, C.; Bergman, J.; Liedberg, B. *J. Phys. Chem.* **1991,** *95*, 3123–3128.

27 Strauss, U. P.; Barbieri, U. P.; Wong, G. *J. Phys. Chem.* **1979,** *83*, 2840–2843.

28 Po, H. N.; Senozan, N. M. *J. Chem. Educ.* **2001,** *78*, 1499–1503.

29 Catalan, J.; Abloud, J. L. M.; Elguero, J. *Adv. Heterocycl. Chem.* **1987,** *41*, 187–274.

30 Mazyar, N. L.; Annenkov, V. V.; Kruglova, V. A.; Ananiev, S. M.; Danilovtseva, E. N.; Rokhin, A. V.; Zinchenko, S. V. *Russ. Chem. Bull.* **2000,** *49*, 2013–2017.