

Chemical Modification of Poly(vinylacetylene) and Synthesis of Poly(1,2,3-triazole)s

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A series of new polymers containing 1,2,3-triazoles were synthesized and their structures and properties were characterized by FT-IR, ¹H NMR, TGA, DSC and GPC. The results showed that the polymers modified by alkyl groups had good solubility, thermal stability and reasonable molecular weights. It was also demonstrated that the properties of fluorine-containing polymers were seriously affected by fluorine atoms with hydrophobic and chemical proof properties.

Key Words : Chemical modification, 1,2,3-Triazoles, Fluorinated polymers, Properties

Introduction

In recent years, there has been wide interests in click chemistry, an appealing concept proposed by Sharpless and co-workers,¹ especially the copper-catalyzed Huisgen 1,3-dipolar cycloaddition of azides and terminal alkynes, the archetypal example of click chemistry. Since the objective of click chemistry would be to establish an ideal set of straightforward and highly selective reactions in synthetic chemistry, more and more researchers have been engaged in developing this strategy. In the field of polymer materials, click chemistry has been used for polymeric synthesis as well as the modification of surfaces nanometer- and meso-scale structures.² Click reaction was used for synthesis of polymers containing 1,2,3-triazoles in the backbones from the monomers of dialkynes and diazides. For example, a new kind of glue was obtained with click chemistry by Diaz *et al.*³ and a series of poly(alkyl aryl) ethers were synthesized with click chemistry reaction in our research group.⁴ And functional hyperbranched polymers were synthesized by click reaction from the monomers of triynes and diazides.⁵ When click reaction was applied in the chemical modification of polymers, many novel polymers were also obtained such as dendronized polymers,⁶ hydrogels,⁷ end-functional polymers,⁸ and so on..

The preparation of Poly(vinylacetylene) (PVacet) was firstly reported by Kaneko *et al.*⁹ and then a few reports on PVacet were occurrence.¹⁰ To the best of our knowledge, however, no report on its thermal stability has been yet available. In fact, it would explode at 210 °C, which was demonstrated by thermogravimetric analysis in this report. So the pendent terminal alkynes in PVacet were used to react with azides *via* click reaction to get some modified polymers that we expected. In this paper, the thermal stability of PVacet and modified PVacet with pendent alkyl or fluoro-alkyl groups were studied. Meanwhile, the 1,2,3-triazole rings grafted onto the substrate polymer may increase the antibacterial ability of novel polymers.¹¹ And due to the

characteristics of fluorine atoms, the enhanced appearance of fluorinated portions on the surfaces of fluorine-containing polymers is of importance in the potential applications as anti-thermal, water repellency, chemical proof, lubricant and electric insulation materials.¹²

Experimental Part

Materials. Triethylamine (TEA), tetrahydrofuran (THF), methanol (MeOH) and acetonitrile (MeCN) were distilled from CaH₂. Chlorotrimethylsilane was distilled from P₂O₅. Magnesium turnings were treated with 5% aqueous hydrochloric acid for several minutes, washed with water, ethanol and ether successively, and dried at 120 °C under vacuum for 4 h. Other reagents were used as supplied. Trimethylsilylacetylene (TMSA) **1** was synthesized from commercial acetylene using literature procedures.¹³

Measurements. Infrared spectra were obtained on Thermo Electron Corporation Nicolet 380 FT-IR spectrophotometer. ¹H NMR (400 MHz) was recorded on a Bruker AM-400 spectrometer with Me₄Si (¹H NMR) as an internal standard. Relative molecular weights and molecular weight distributions were measured by gel permeation chromatography (GPC) system equipped with a Waters 1515 Isocratic HPLC pump, a Waters 2414 refractive index detector (RI), a Waters 2487 dual-wavelength λ absorbance detector and a set of Waters Styragel columns (HR3, HR4 and HR5, 7.8 × 300 mm). GPC measurements were carried out at 35 °C using THF as an eluent with a 1.0 mL/min flow rate. The system was calibrated with polystyrene standards. Differential scanning calorimetry (DSC) was conducted on a NetZSch (German) DSC 204 F1 system under nitrogen calibrated with indium and zinc standards. Thermogravimetric analysis (TGA) was performed on NetZSch (German) TGA 209 F1 system on powder samples at a heating rate of 10 °C/min in N₂ atmosphere.

Synthesis of PVacet 4. PVacet was prepared through three steps and the detailed procedures were reported by Helms.⁶

Polymer 3: white powder (80%). IR (KBr, cm^{-1}): ν 2959, 2917, 2899, 2852, 2168, 1944, 1865, 1447, 1407, 1350, 1250, 1098, 841, 759, 698, 638; $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 2.9-2.6 (1H, br), 1.6-1.2 (2H, br), 0.2 (9H, s).

Polymer 4: pale yellow powder (72%). IR (KBr, cm^{-1}): ν 3299, 2928, 2856, 2113, 1629, 1448, 1363, 1253, 1098, 848, 630; $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 3.2-2.7 (1H, br), 2.12 (1H, s), 1.9-1.4 (2H, br). Mn = 30150, Mw = 69600, PDI = 2.31.

Synthesis of Alkyl and Fluoroalkyl Azides from Halides 5a-c. To a 50 mL three-necked flask equipped with a magnetic stirrer, a thermometer and a condenser were added alkyl bromide or fluoroalkyl iodide (5 mmol), NaN_3 (390 mg, 6 mmol) dissolved in 10 mL water and Tetrabutylammonium bromide (32 mg, 2 mol %). The reaction mixture was stirred at 90 °C for 24 h and then cooled to room temperature, and extracted with ether (3×10 mL). The organic phase was dried over MgSO_4 , filtered, and concentrated. The products **5a-c** were obtained by flash chromatography based on gel silica with petroleum ether/ethyl acetate (10:1 v/v) as the eluent.

Compound 5a: colorless liquid (450 mg, 91%). IR (KBr, cm^{-1}): ν 2962, 2925, 2854, 2103, 1629, 1458, 1412, 1260, 1094, 1019, 863, 800; $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 3.47 (2H, m, $J = 7.01$ Hz), 1.55 (2H, m, $J = 6.72$ Hz, $J = 7.54$ Hz), 1.38 (2H, m, $J = 7.01$ Hz, $J = 7.54$ Hz), 0.93 (3H, m, $J = 6.68$ Hz).

Compound 5b: colorless liquid (713 mg, 92%). IR (KBr, cm^{-1}): ν 2926, 2857, 2096, 1555, 1459, 1374, 1260, 1104, 1023, 804; $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 3.25 (2H, m, $J = 7.01$ Hz), 1.58 (2H, m, $J = 7.01$ Hz, $J = 7.53$ Hz), 1.35 (10H, m), 0.89 (3H, t, $J = 7.01$ Hz).

Compound 5c: white solid (2.32 g, 95%). IR (KBr, cm^{-1}): ν 2960, 2922, 2856, 2109, 1629, 1444, 1343, 1206, 1151, 1079, 1066, 986, 921, 882, 711; $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 3.62 (2H, m, $J = 7.01$ Hz), 2.55 (2H, m, $J = 7.01$ Hz).

Synthesis of 2,2,2-trifluoroethyl Azide 5d. Methanesulfonyl chloride (228 mg, 2 mmol) was slowly dropped, under a nitrogen atmosphere, to a dichloride methane solution (30 mL) of trifluoroethanol (200 mg, 2 mmol) and triethylamine (10 mg, 5 mol %) at -5 °C. After complete methanesulfonylation (4 h), the solvent was removed by rotary evaporation. Then, to this system, NaN_3 (143 mg, 2.2 mmol), DMSO (30 mL) and 18-crown-6 (27 mg, 5 mol %) were added, and stirred at 110 °C for 20 h. The reaction mixture was diluted with ether (50 mL) and washed with brine (3×10 mL) followed by water (3×10 mL). The organic phase was dried over MgSO_4 , filtered, and concentrated. The product **5d** was obtained by flash chromatography based on gel silica with petroleum ether/ethyl acetate (10:1 v/v) as the eluent.¹⁴

Compound 5d: pale brown liquid (208 mg, 85%). IR (KBr, cm^{-1}): ν 2960, 2922, 2856, 2109, 1629, 1444, 1343, 1206, 1151, 1079, 1066, 986, 921, 882, 711; $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 3.85 (2H, dd).

Chemical Modification of Polymers. To a 25 mL flask equipped with a magnetic stirrer were added PVacet (30 mg,

0.58 mmol) and organic azide (0.58 mmol) dissolved in 8 mL THF. Under vigorously stirring, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ (7 mg, 5 mol %) and sodium ascorbate (12 mg, 10 mol %) dissolved in 8 mL H_2O were added, then stirred for 12 h at room temperature. The reaction mixture was poured into hexane, and the precipitate was washed with ammonia and water for several times. Finally, the products were dried at 60 °C under vacuum for 48 h.

Compound 6a: pale solid powder (64 mg, 73%). IR (KBr, cm^{-1}): ν 3131, 3063, 2958, 2934, 2873, 1637, 1542, 1458, 1380, 1336, 1247, 1216, 1146, 1095, 1051, 835, 802, 757; $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 6.9-7.2 (1H, br), 1.4-1.1 (2H, br), 4.4-3.9 (2H, br), 2.4-2.1 (1H, br), 1.9-1.5 (4H, br), 1.0-0.8 (3H, br); Mn = 51230, Mw = 135800, PDI = 2.65.

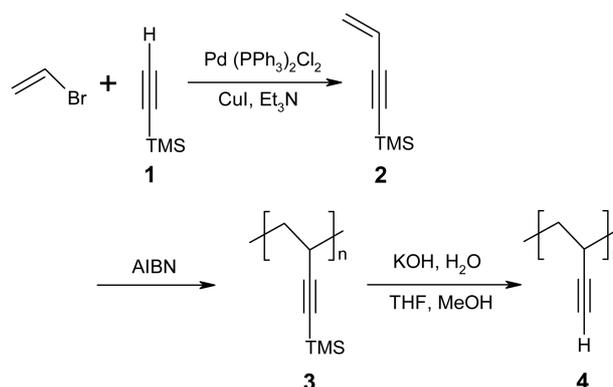
Compound 6b: pale solid powder (76 mg, 64%). IR (KBr, cm^{-1}): ν 3125, 3064, 2927, 2856, 1631, 1538, 1458, 1340, 1261, 1216, 1152, 1105, 1045, 906, 858, 803, 726; $^1\text{H NMR}$ (400 MHz, CDCl_3 , δ): 7.2-6.8 (1H, br), 4.4-4.0 (2H, br), 2.4-2.1 (1H, br), 2.0-1.5 (2H, br), 1.5-1.0 (12H, br), 1.0-0.7 (3H, br); Mn = 63856, Mw = 175600, PDI = 2.75.

Compound 6c: yellow solid powder (186 mg, 60%). IR (KBr, cm^{-1}): ν 3124, 3060, 2945, 2855, 1635, 1457, 1212, 1151, 992, 841, 808, 737.

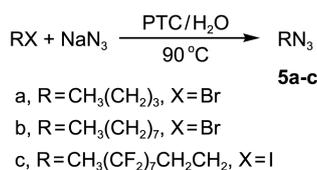
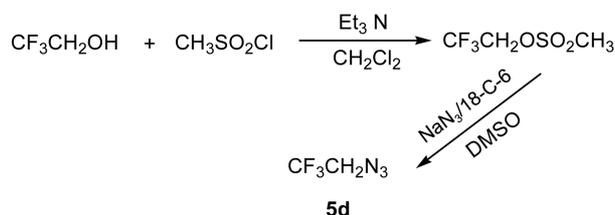
Compound 6d: yellow solid powder (62 mg, 80%). IR (KBr, cm^{-1}): ν 3125, 3061, 2933, 2855, 2109, 1636, 1457, 1396, 1336, 1266, 1170, 1096, 1046, 930, 838, 798.

Results and Discussion

Synthesis and Characterization of PVacet. PVacet was prepared according to the literature procedures (Scheme 1).⁶ First, compound **2** was synthesized by the Sonogashira coupling reaction¹⁵ between vinyl bromide and trimethylsilylacetylene (TMSA) in which 5 mol % $\text{Pd}(\text{PPh}_3)_2\text{Cl}_2$ was used as a typical palladium catalyst, 10 mol % CuI as a cocatalyst, and triethylamine as a solvent with a yield of 60%. Then, the monomer **2** was polymerized in bulk at 60 °C with AIBN. No fraction of the TMS-protected polymer **3** was performed in this procedure, which resulted in broader polydispersity than that described in the literature. Finally, the polymer **3** was dissolved in THF and deprotected under aqueous KOH to produce polymer **4** containing pendent alkynes.



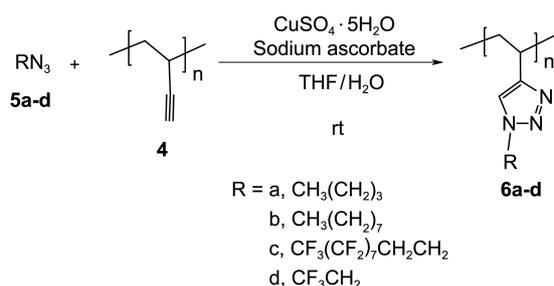
Scheme 1. Synthesis of PVacet.

**Scheme 2.** Synthesis of organic azides.**Scheme 3.** Synthesis of azido trifluoroethane.

Synthesis of Organic Azides. Organic azides can be prepared from halides, alcohols, amines or hydrazines.¹⁶ Here, the azides **5a-c** were synthesized through modification of literature procedures¹⁷ in 85-95% yields by halides (Scheme 2). In the reactions performed in our lab, rather than organic solvent, only water was added and tetrabutylammonium bromide was used as a kind of phase transfer catalyst (PTC), which resulted in a little higher yields and easy purification. As for the preparation of compound **5d**, two steps were required with 2,2,2-trifluoro-ethanol as the original material (Scheme 3). At first, the intermediate, methylsulfonyl ramification was formed, and then the resulting ramification reacted with NaN₃ without further purification.¹⁸

Chemical Modification of PVacet. The chemical modification of PVacet were carried out in a 1:1 solvent ratio of water to THF using 5 mol % CuSO₄·5H₂O and 10 mol % sodium ascorbate (Scheme 4). Usually, the click reactions were performed smoothly at room temperature. When we raised the temperature to 60 °C, the reaction would be completed in an hour, but the resultant molecular weight distribution was not as good as what we had got at room temperature. The difference of the isolated yields of polymers **6a-d** might be attributed to the bulk effect of azides: the larger the volume of organic azide was, the lower the yield could be. The change of the color of the solution, from orange yellow to blue green, was a simple signal for the completion of the reaction.

Properties of Polymers.

**Scheme 4.** Modification of polymers by click chemistry.**Table 1.** Solubility of PVacet and the modified polymers

Polymers	Acetone	THF	CHCl ₃	NMP	DMSO	DMF
4	+	+	+	+	+	+
6a	+	+	+	+	+	+
6b	+	+	+	+	+	+
6c	-	-	-	s	s	s
6d	-	-	-	-	-	-

Note: (+), soluble; (s), swell; (-), insoluble.

Table 2. Physical properties of PVacet and the modified polymers

Polymers	Mn ^a	Mw ^a	(Mw/Mn) ^a	T _g ^b (°C)	T _d ^b (°C)
4	30150	69600	2.31	52	210
6a	51230	135800	2.65	86	314
6b	63860	175600	2.75	-	287
6c	-	-	-	65	336
6d	-	-	-	-	439

^aGPC in THF (0.1 wt %) vs. polystyrene at 35 °C. ^bDSC and TGA at 10 °C/min in N₂ atmosphere.

Solubility of Polymers: From the solubility tests of polymers (Table 1), we can see that polymers **6a** and **6b** possessed good solubility which might be the result of grafting flexible pendent groups onto substrate polymer, but polymers **6c** and **6d** containing fluorine atoms were not able to be dissolved in most organic solvents such as acetone, THF, CHCl₃, DMF, and so on. Polymer **6c** only could be swollen in the polar solvents, and **6d** could be dispersed homogeneously in the polar solvents, but it would subside after keeping immobile for a period of time. The chemical proof property of modified polymers **6c** and **6d** might be illustrated that the pendent fluorinated groups, like a sheath, protected the backbones of polymers from the attack of organic solvents.

Molecular Weights and Their Distributions of Polymers: The molecular weights and their distributions of PVacet and modified polymers were listed in the Table 2. It can be seen that the molecular weights of modified polymers **6a** and **6b**, determined by GPC, became larger and the molecular weight distributions became a little broader. Furthermore, the molecular weights of polymers became heavier with the increase of the molecular weights of pendent chains, which was similar to what was described by Helms.⁷ However, fluorinated polymers **6c** and **6d** couldn't be characterized by GPC because of their insolubility in organic solvents such as acetone, THF, DMF, and so on.

Thermal Stability of Polymers: The thermal stability of each polymer were examined with dynamic thermogravimetric analysis (TGA) at a heating rate of 10 °C/min (Fig. 1). Corresponding decomposed temperatures (T_d) were listed in the Table 2. It should be noted that the substrate polymer, PVacet showed a volatile weight loss at about 210 °C. To demonstrate this exploding case, a small block of PVacet was placed in a Bunsen burner flame and it blew up with a "pu" sound. However, all the modified polymers displayed good thermal stability. The fluorinated polymers **6c-d** ex-

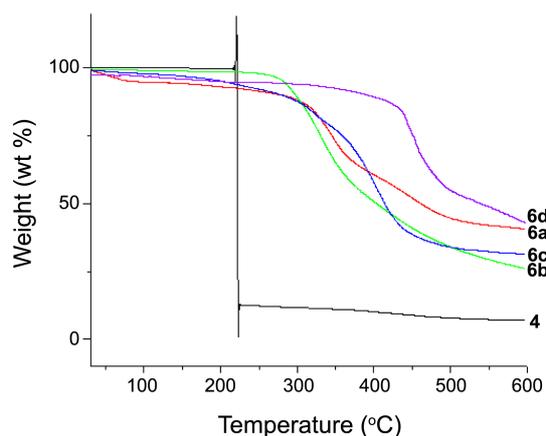


Figure 1. TG curves of polymers.

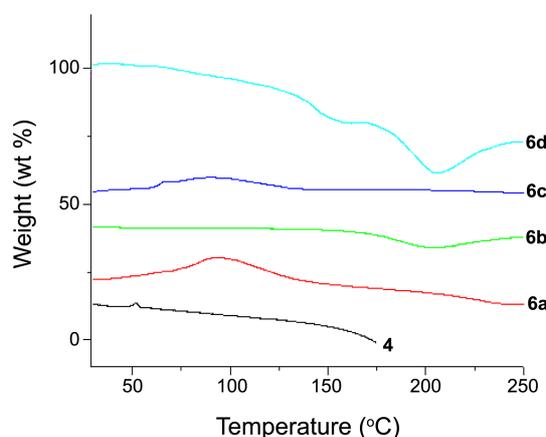


Figure 2. DSC curves of polymers with endo direction.

hibited higher T_d value than those of the polymers **6a-b** because of the stronger interchain interactions of the $-\text{CF}_3$ groups. The polymer **6d** exhibited much higher T_d value than that of the polymer **6c**, and this was attributed to the longer fluorine-containing pendant chains in the polymer **6d**.

The series of polymers were subjected to different scanning calorimetry (DSC), and the results of these experiments are shown in Figure 2 and Table 2. The polymers showed weak glass transitions, some of which could not be assigned unambiguously. Because of the instability of the substrate polymer **4**, the terminal measurement temperature was stopped at 180 °C, before which there was no occurrence of crystallization peak or melting peak in DSC curve. The T_g 's values of polymers **6a** and **6c** were higher than that of the precursor **4**, which was attributable to the rigid properties of 1,2,3-triazole rings. Exothermic peaks were observed on the

curves of polymers **6b** and **6d** from 150 °C to 230 °C, and this might be attributed to the cooling crystallization of the long pendant units.

Conclusions

PVAcet was prepared through three steps from TMSA, and then it was modified *via* click reaction with the introduction of alkyl or fluoroalkyl groups to the pendent alkynes of the polymer. The solubility of alkyl-modified polymers was the same as PVAcet, but the thermal stability was greatly improved. Fluoroalkyl-modified polymers, with excellent thermal stability and solvent-repelling, could have potential applications as anti-thermal, water repellency and chemical proof materials.

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- Caution: Be careful in the operation of organic azides which were facile to explode. Don't evaporate to dryness in the process of rotary evaporation!