

Rapid Communication

SYNTHESIS OF POLYELECTROLYTIC POLYACETYLENE DERIVATIVES BY QUATERNIZATION OF POLY(PYRIDYLACETYLENE)*

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Abstract Functional polyacetylenes containing pyridinium side groups (PPyA-MX, X = Br and I) were successfully synthesized. Spectroscopic techniques such as ¹H-NMR, ¹³C-NMR, and FTIR spectroscopy were used to characterize the structure of the obtained polymers. The characterization data were well consistent with the expected macromolecular structures. PPyA-MI had good solubility in polar organic solvents and low solubility in water, while PPyA-MBr had good solubility in both polar organic solvents and water.

Keywords: Polyacetylene derivative; Polyelectrolyte; Characterization; Water solubility; Thermal stability.

Polyacetylene is the prototypical conjugated polymer, its functional derivatives have shown versatile and promising properties such as electrical and photoconductivity, liquid crystal property, gas permeability, chiral recognition, supramolecular assemblies, formation of helical graphitic nanofibers, as summarized in comprehensive reviews^[1–5]. We investigated the synthesis of a series of functional polyacetylenes and the preparation of their composites with inorganic components including perovskite structures^[6], inorganic nanostructures^[7–10] and especially carbon nanotubes^[9–18]. A representative work was the wrapping of amino-functionalized polyphenylacetylene (amino-PPA) chains onto the multiwalled carbon nanotubes (MWNTs), which afforded the desirable dispersion of MWCNTs in acidic aqueous solutions. By aid of the amino groups and solubility in aqueous media, the amino-PPA/MWNTs hybrids were used as template to decorate silver, zinc oxide and γ -Fe₃O₄ nanoparticles on the surface of MWNTs through wet-chemistry method. As demonstrated in the literature^[10], the realization of the water solubility provides a strategy to prepare multi-component composites.

In the above-mentioned case, the amino-PPA can only be dissolved in acidic solutions with the help of protonation of amino groups. This limits the application of the functionalized polyacetylenes in various situations. It is reasonable that intrinsic water soluble polyacetylenes, *i.e.* polyelectrolyte polyacetylene (PE-PA)

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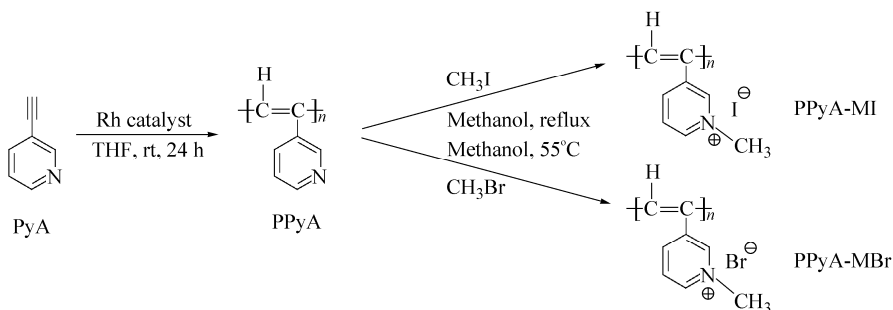
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derivatives are more fundamentally and practically demanding. But in fact, PE-PA derivatives have been rarely reported so far^[19–23]. Herein, we report our strategy to prepare PE-PA derivatives by quaternization of poly(pyridylacetylene). The *meta*-acetyl-pyridine is chosen as monomer and was polymerized in the presence of Rh-catalyst. After quaternization with bromo- and iodomethane, the polymers carry Br[−] or I[−] anions, which bestow the polymers with acceptable water solubility.

The synthetic route to the expected PE-PA derivatives is shown in Scheme 1. A brief description of the synthesis procedures is as following. The catalysts (including [Rh(nbd)Cl]₂ and [Rh(cod)Cl]₂) were prepared in our laboratory following the literature method^[24, 25]. CH₃I, CH₃Br, and solvents dichloromethane (DCM), dimethylsulfoxide (DMSO) and *N,N*-dimethylformamide (DMF) were all in AR grade and purchased from the National Chemicals Co. Ltd.; except for CH₃I, which was distilled before using, other chemicals were used as received without further purification. Into a 20 mL Schlenk tube with a side arm was placed 300 mg (2.9 mmol) of *meta*-acetyl-pyridine (99%, purchased from Aldrich). The tube was evacuated under vacuum and then flushed with nitrogen three times through the side arm. Then 5 mL of dry THF (distilled under normal pressure from sodium benzophenone ketyl under argon immediately prior to use) was injected. The catalyst solution was prepared in another Schlenk tube by dissolving 8.0 mg of Rh⁺(nbd) [C₆H₅B[−](C₆H₅)₃] in 3 mL of dry THF. After aging for 15 min, it was transferred into the monomer solution by using a hypodermic syringe. The reaction mixture was stirred at room temperature under nitrogen for 24 h. The resulting mixture was diluted with 6 mL of THF and added dropwise into 500 mL of hexane under stirring. After keeping still over night, the precipitate was filtered with a Gooch crucible. The polymer was re-dissolved in THF and precipitated in hexane for three times. Finally, the solid was collected and dried in a vacuum oven at 40°C to a constant weight. Characterization data: dark yellow solid; yield: 65.2%. *M*_w: 42100, *M*_w/*M*_n: 1.10. IR (KBr), ν (cm^{−1}): 2965, 1374, 1356, 1265, 1194, 1154, 1076, 1016, 813, 699. ¹H-NMR (300 MHz, DMSO-*d*₆), δ (TMS): 8.32, 8.08, 7.52–6.57 (pyridyl-H), 5.79 (CH=C). ¹³C-NMR (75 MHz, DMSO-*d*₆), δ (TMS): 149.0, 148.2, 136.8, 134.3, 123.1 (pyridyl-C); 137.7 (CH=C-Pyridyl); 132.0 (HC=C-Pyridyl).



Scheme 1 Synthetic routes to PE-PA derivatives

The quaternization of PPyA is briefly described as below as an example. Into a 100 mL flask equipped with a condenser was added 200 mg (*ca.* 1.94 mmol) of PPyA, 300 mg CH₃I and 30 mL absolute methanol. The reaction system was refluxed for 6 h in a N₂ atmosphere. Then, the resultant mixture was cooled to room temperature. After removal of the solvent and CH₃I, the crude product was vacuum evaporated. 10 mL DMSO was introduced into the flask to dissolve the residue. The solution was dropwise added to 500 mL of ether. The suspension was kept still over night; then the precipitate was filtered with a Gooch crucible. The solid was re-dissolved in DMSO and precipitated in ether twice. The resultant was dried in a vacuum oven at 40°C to a constant weight. Characterization data: PPyA-MI: dark brown solid; yield: 99.8%. IR (KBr), ν (cm^{−1}): 2965, 1374, 1356, 1265, 1194, 1154, 1076, 1016, 813, 699. ¹H-NMR (300 MHz, DMSO-*d*₆), δ (TMS): 9.31, 8.77, 8.64, 8.02 (pyridyl-H), 6.83 (CH=C), 4.23 (−CH₃). ¹³C-NMR (75 MHz, DMSO-*d*₆), δ (TMS): 146.2–142.3 (pyridyl-C), 137.1–132.9 (CH=C-Pyridyl, pyridyl-C), 128.7–125.4 (HC=C-Pyridyl, pyridyl-C); 48.5 (CH₃). PPyA-MBr: dark brown solid; yield: 97.3%. ¹H-NMR (300 MHz, D₂O), δ (TMS): 8.91 (Pyridyl-H, at

2 position), 8.41 (Pyr-H, at 4 and 6 positions), 7.85 (Pyr-H, at 5 position), 6.52 (HC=), 4.13 (CH₃). ¹³C-NMR (100 MHz, D₂O), δ (TMS): 146–125 (Pyr-C, at 2, 3, 4, 5, 6 positions; HC=CPyr), 48 (CH₃).

In our previous work, we also found that polyacetylene derivatives bearing a thiol or an amino functional groups could not be directly prepared by using Rh-catalysts because the polymerization could not propagate or the resultant was intractable^[7–9]. Considering that [Rh(nbd)Cl]₂ and [Rh(cod)Cl]₂ have been proved to be highly effective catalysts for phenylacetylene derivatives to produce polymers with *cis*-rich regioregularity, we first tried to use [Rh(nbd)Cl]₂ to polymerize *meta*-acetylpyridine in DCM and THF, respectively. At the beginning of the polymerization, the reaction mixture in the tube was homogenous. However, only after a few of minutes, yellow brown solution was formed and the resultant precipitated from the solvent. As revealed by the data in Table 1, the solid products are insoluble in common organic solvents, though their yields are rather high. According to the experiment observations, it seems that the polymerization can be accelerated by the monomer itself. This is reasonable because triethylamine (TEA, distilled and dried over potassium hydroxide) is a good assistant catalyst usually used for helping the polymerization of phenylacetylene-based monomers in the cases of [Rh(nbd)Cl]₂ or [Rh(cod)Cl]₂ being used as catalyst, and pyridine itself is a kind of organic alkali. Moreover, Blumstein and co-workers reported that the *N*-alkyl-*ortho*- and *N*-alkyl-*para*-ethynylpyridiniums were sufficiently active that they underwent spontaneous polymerization^[19, 20]. Recently, the activated polymerization of 2-ethynylpyridine by using 4-(methylthio)benzyl bromide as quaternization agent was reported by Kwak *et al.*, the polymerization proceeded well in polar solvents without any additional initiator and catalyst^[23]. In our experiments, we also prepared *N*-methyl-*meta*-ethynylpyridinium iodine, but this monomer was not as active as *ortho*- and *para*-ethynylpyridinium halide; it was stable in polar solvents and did not polymerized spontaneously. This is reasonable that a substitution at *para*- or *ortho*-position of benzene always has stronger electronic (push or pull) effect than that at *meta*-position.

Table 1. Polymerization of *meta*-ethynylpyridine^a

No.	Catalyst ^b	Solvent	Yield (%)	M_w^c	M_w/M_n^c
1	[Rh(cod)Cl] ₂	DCM	82.0	d	d
2	[Rh(cod)Cl] ₂	THF	73.0	d	d
3	[Rh(nbd)Cl] ₂	DCM	86.0	d	d
4	[Rh(nbd)Cl] ₂	THF	74.0	d	d
5	Rh ⁺ [η^6 -C ₆ H ₅ (nbd)B [−] (C ₆ H ₅) ₃]	THF	65.0	42100	1.10

^a Carried out at room temperature in an atmosphere of dry nitrogen for 24 h; [M]₀ = 0.2 mol/L, [cat.] = 2 mmol/L;

^b cod = 1,5-cyclooctadiene; nbd = 2,5-norbornadiene. For [Rh(cod)Cl]₂ and [Rh(nbd)Cl]₂, one drop of TEA was used;

^c Determined by GPC (Waters associated gel permeation chromatography system) in THF on the basis of a polystyrene calibration;

^d Insoluble in common organic solvents

To obtain soluble target polymers, we turned our attention to the zwitterionic catalyst Rh⁺(nbd)[C₆H₅B[−](C₆H₅)₃], which was used to successfully polymerize thiol- and amino-containing phenylacetylenic monomers. Delightfully, the reaction mixture was homogeneous through the polymerization, and the resulting polymer became soluble in some common organic solvents such as THF, DCM, DMF and DMSO. In comparison to DCM, DMSO and THF are better solvents, probably because the zwitterionic Rh-complex likes the hydrophilic, polar solvents. The good solubility offered us the possibility to characterize the polymer's structure and properties. The target polymer PPyA with a molecular weight of 42100 and a PDI of 1.10 was obtained in a yield of 65%. The quaternization of PPyA by reacting the polymer with CH₃I went smoothly and efficiently. As revealed by the characterization data, the yield was 99.8%, approximately all pyridine moieties had been transformed into salt. This was also confirmed by the spectroscopic data shown below.

Spectroscopic methods such as IR (on a Bruker VECTOR 22 spectrometer), ¹H-NMR and ¹³C-NMR

spectra (a Bruker ARX 500 spectrometer) were used to examine the chemical structure of the obtained polymers. All the polymers as well as their monomers gave satisfactory analysis data corresponding to their expected molecular structures. IR spectra of PPyA and PPyA-MI are depicted in Fig. 1; the IR spectrum of the monomer PyA is also given in the same figure for comparison. On curve (a), the absorption bands at 3285 and 2103 cm^{-1} can be assigned to the stretching vibrations of $\equiv\text{C}-\text{H}$ and $\text{C}\equiv\text{C}$, respectively. These two bands vanished on curve (b), corresponding to the IR spectrum of PPyA, indicating that the triple bond in the monomer has been fully consumed by the polymerization reaction. On curve (c), two bands at 2977 and 2926 cm^{-1} can be observed and assigned to the stretching vibrations of $-\text{CH}_3$ groups, indicating the successful quaternization of the pyridine moieties of PPyA with iodomethane. Meanwhile, for PPyA-MI, the absorption pattern in the region from 1650 cm^{-1} to 1350 cm^{-1} is quite different from PPyA. Especially, the absorption at 1622 cm^{-1} , associating with the stretching of $\text{C}=\text{C}$ bond, enhances evidently when PPyA is transformed into PPyA-MI. These changes imply that the quaternization of pyridyl moieties modifies the correlation between the polyene backbone and the pyridyl pendants.

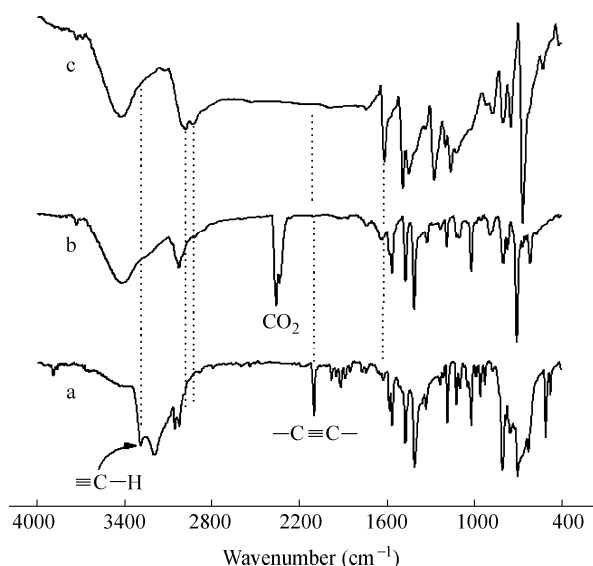


Fig. 1 FT-IR spectra of the monomer PyA (a), its polymer PPyA (b) and the quaternized resultant PPyA-MI (c)

To further confirm the polymerization and quaternization have been successfully realized, the ^1H -NMR, ^{13}C -NMR and UV-Visible spectra of the monomer and polymers were measured (see Figs. 2 and 3). As shown in Fig. 2, the resonance peak at $\delta = 3.2$ is assigned to the chemical shift of the proton direct bonding to $\text{C}\equiv\text{C}$ group (spectrum A). This peak disappears in the spectrum of the resulted polymer PPyA (curve C). Meanwhile, a new peak appears at δ ca. 5.8, which can be assigned to the chemical shift of olefinic protons. For monomer, the resonance peaks for the protons on the pyridyl ring show in the region from δ ca. 7.22 to 8.78; while for polymer, the relevant peaks shift to the region from δ ca. 6.96 to 8.36. At the same time, the peaks for the polymer are wider than those for monomer. The high-field shift of the resonance peaks suggests the conjugation of the pyridyl groups with the polyene backbone, and peak broadening implies the interplaying of the adjacent segments, thereby the formation of polymer chains. All these data indicate the triple bond has been transformed into double bond and the monomers have been polymerized. In ^1H -NMR spectrum of PPyA-MI (Fig. 2D), there is a singlet peak at δ ca. 4.2. It is assigned to the protons of the methyl groups connecting to pyridyl side groups. The emergence of this peak indicates the quaternization has been achieved. In comparison with PPyA, the resonance peaks of the protons on polyene-backbone and pyridyl side-group of PPyA-MI shift to low field. This spectral change is associated with the quaternization of the pyridine moiety. A similar effect is also observed for

the quaternized monomer (Fig. 2B). Moreover, a quantitative comparison of the integrated area of peak a with that of f (or peak c with peak f) finds out that the ratio is 1:3. In addition, no resonance peaks corresponding to pristine pyridyl groups can be found on spectrum (D). These results mean all the pyridyl side groups on PPyA have been quaternized by iodomethane. Such a conclusion is also confirmed by the fact that the extremely high yield of PPyA-MI from PPyA is obtained.

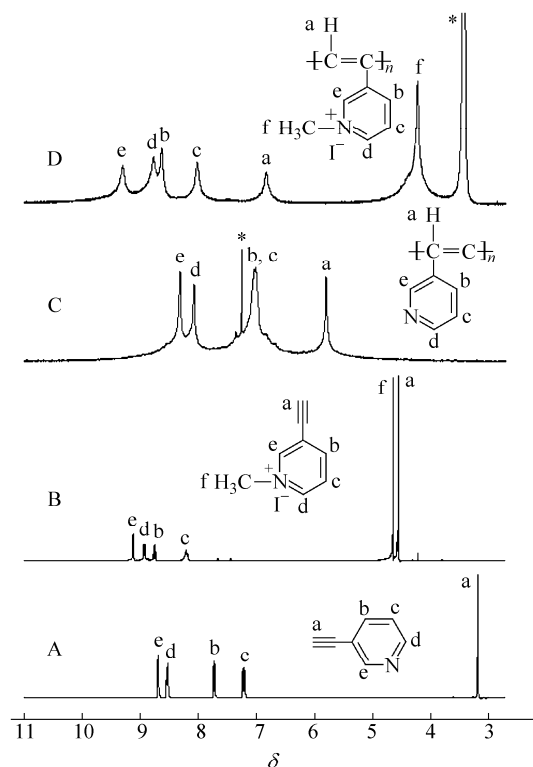


Fig. 2 ^1H -NMR spectra of the monomer PyA in chloroform- d (A), PyA-MI in D_2O (B), the polymer PPyA in chloroform- d (C) and the quaternized polymer PPyA-MI in $\text{DMSO}-d_6$ (D). The solvent peaks are marked with asterisks.

The chemical structures of the monomer, PPyA and PPyA-MI have also been characterized by ^{13}C -NMR spectroscopy and the results are shown in Fig. 3. Whereas the acetylenic carbon atoms of the monomer resonate at δ ca. 80.5 ($\equiv\text{C}$ -pyridyl) and 80.1 ($\text{HC}\equiv$), these peaks are completely lost in the spectra of PPyA and PPyA-MI. The carbon atoms of the olefin backbone of PPyA appear at δ ca. 137.6 ($=\text{C}$ -pyridyl) and 132.1 ($\text{HC}=\text{C}$); but for PPyA, these peaks cannot be well-distinguished, due to their overlapping with the carbon resonances of pyridyl side groups, which implies the good conjugation between the pyridyl side group and olefinic main-chain. The conjugation effect is also reflected by the low-field shift of the resonance of carbon c from δ ca. 119.1 to 136.8. These observations are in good consistent with our previous results^[26, 27]. On the spectrum of PPyA-MI, a resonance peak appears at δ ca. 48.3, which is assigned to the signal from the carbon atoms in methyl groups. Consequently, the ^{13}C -NMR characterization results sufficiently support the conclusion that expected polymers, *i.e.* PPyA and PPyA-MI have been obtained.

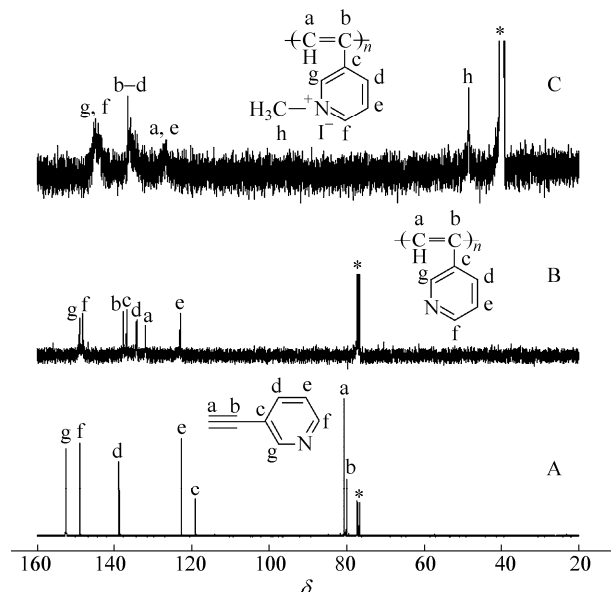


Fig. 3 ^{13}C -NMR spectra of PyA (A), its polymer PPyA in chloroform- d (B) and PPyA-MI in $\text{DMSO}-d_6$ (C). The solvent peaks are marked with asterisks.

The resultant polymers of PPyA-MI and PPyA-MBr can be considered as polyelectrolytes because of the quaternization of the pyridyl moieties. We tried the solubility of PPyA, PPyA-MI and PPyA-MBr in different solvents, and the results are summarized in Table 2. It is found that PPyA has desirable solubility in many common solvents such as methanol, DCM, chloroform, DMSO and DMF, but insoluble in water. Its quaternized resultants, PPyA-MI and PPyA-MBr show good solubility in DMSO and DMF; but these ionic polyacetylene derivatives, unlike common polyelectrolyte, are only partially soluble in water. At room temperature, the absolute solubility for PPyA-MI is only about 0.25 mg/mL; while the solubility of PPyA-MBr in water is as high as 15 mg/mL. The pronounced difference in water-solubility of PPyA-MI and PPyA-MBr may be ascribed to the stronger affinity of iodine anions to polyene backbone than that of bromide anions. Anyway, the solubility experiments indicate that both PPyA-MI and PPyA-MBr can be dissolved in water.

Table 2. Relative solubility of the eerived polymers in common solvents

Polymer	H_2O	Methanol	DMF	DMSO	THF	CHCl_3	DCM	Toluene
PPyA	$\ominus$	$\oplus$	$\oplus$	$\oplus$	$\circ$	$\oplus$	$\oplus$	$\ominus$
PPyA-MI	$\circ$	$\oplus$	$\circ$	$\oplus$	$\ominus$	$\ominus$	$\ominus$	$\ominus$
PPyA-MBr	$\oplus$	$\circ$	$\circ$	$\oplus$	$\ominus$	$\circ$	$\ominus$	$\ominus$

Solubility: $\oplus$ = good; $\circ$ = moderate; $\ominus$ = poor

The thermal stability of the obtained polymers was evaluated by TGA measurements (on a Perkin-Elmer Pyris thermogravimetric analyzer TGA 6). As shown in Fig. 4, the T_d value of PPyA, PPyA-MI and PPyA-MBr is 260°C, 310°C and 279°C respectively, where T_d is defined as the temperature at which the sample losses 5% of its original weight. In comparison with the data reported in literatures, PPyA-MI shows the highest T_d value. The TGA thermogram of poly{2-ethynyl- N -[4-(methylthio)benzylpyridinium bromide]} showed a slight weight loss around 100°C and an abrupt weight losses around 230°C^[22]. The authors ascribed the weight loss beginning at around 230°C the decomposition of aromatic substituents and crosslinking of the conjugated polymer system. In an earlier work, Subramanyam and Blumstein reported that, run in a nitrogen atmosphere at a heating rate of 10 K/min, poly[(2- N -dodecylpyridiniumyl)acetylene bromide] and poly[(4- N -dodecylpyridinium)-acetylene

bromide] showed sharp and continuous weight loss at about 250°C and 240°C, respectively^[19]; but no explanations were forwarded to the subtle difference in decomposition temperatures. When longer alkyl chain, or octadecyl was used instead of dodecyl, the decomposition temperature decreased. Poly[(2-*N*-octadecylpyridiniumyl)acetylene bromide] began to lose its weight at about 230°C, and the drop of decomposition temperature was associated with the low thermal stability of the long alkyl chains^[20]. In the present case, the shortest alkyl chain, *i.e.* methyl is attached to pyridinium moiety, and the rigidity and the strong ionic interactions between pyridinium moieties are helpful to the higher thermal stability observed for PPyA-MI and PPyA-MBr.

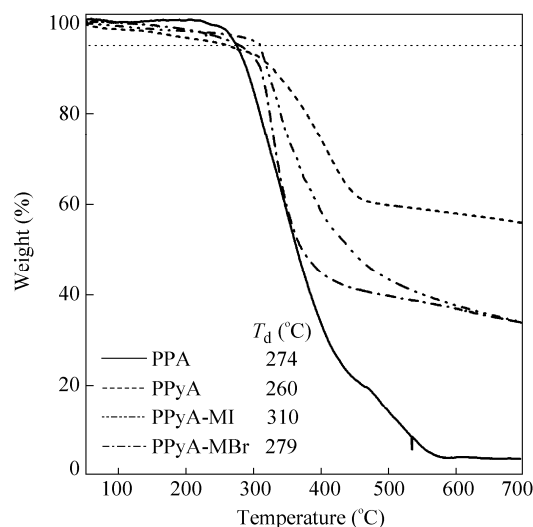


Fig. 4 TGA thermograms of PPA, PPyA, PPyA-MI and PPyA-MBr recorded under nitrogen flow at a heating rate of 20 K/min
 T_d denotes the temperature at which the sample loses 5% of its original weight.

In summary, we have successfully synthesized polyelectrolytic polyacetylene derivatives, PPyA-MBr and PPyA-MI. The chemical structures of these derivatives were fully characterized by spectroscopic techniques such as ¹H-NMR, ¹³C-NMR, and FTIR spectroscopy. The experimental data confirmed the expected macromolecular structures. PPyA-MBr had good solubility both in water and organic solvents; PPyA-MI was highly soluble in polar organic solvents such as DMSO and DMF but partially soluble in water. The derived cationic polymers showed enhanced thermal stability in comparison with polyphenylacetylene and previously reported poly(ethynylpyridine) derivatives.

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