

Supporting Information:

Pyrolysis-gas chromatography-mass spectrometry is an effective method to give clues to identify the macromolecular structure of polymer materials.²⁵ Pyrolysis is designed to break macromolecular chains to small fragments at high temperatures, and these fragments can be separated by gas chromatography and then detected by mass spectrometry. As shown in Fig. S1, PGC-MS chromatogram of PFTP appears three distinctive peaks, which locate at 31.25, 48.02 and 53.14 minutes, respectively. In the mass spectrum of the compound at 31.25, 48.02 and 53.14 minutes, the compound have a molecular ion at m/e 245.08, 336.08 and 412.11, which just corresponds to triphenylamine, *N,N,N'*-triphenyl-benzene-1,4-diamine and *N,N,N,N*-tetraphenylphenylenediamine, respectively. And triphenylamine, *N,N,N'*-triphenyl-benzene-1,4-diamine and *N,N,N,N*-tetraphenylphenylenediamine all are the main possible fragments of PFTP.

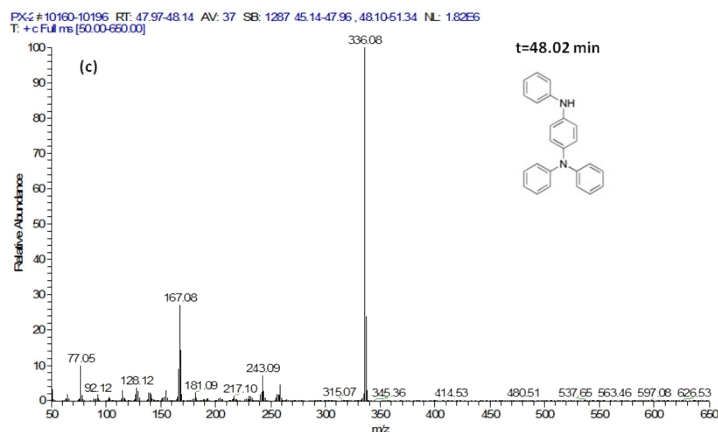
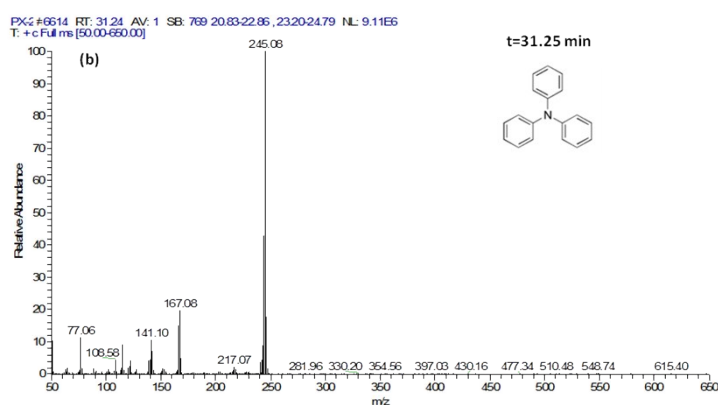
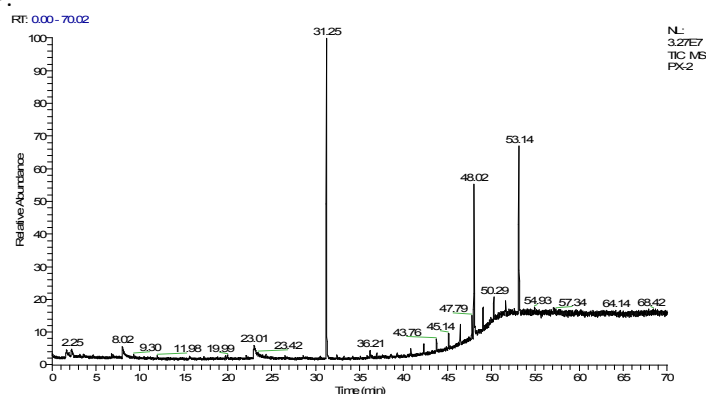


Fig. S1-3 Mass spectrum of the compound at 48.02 min.

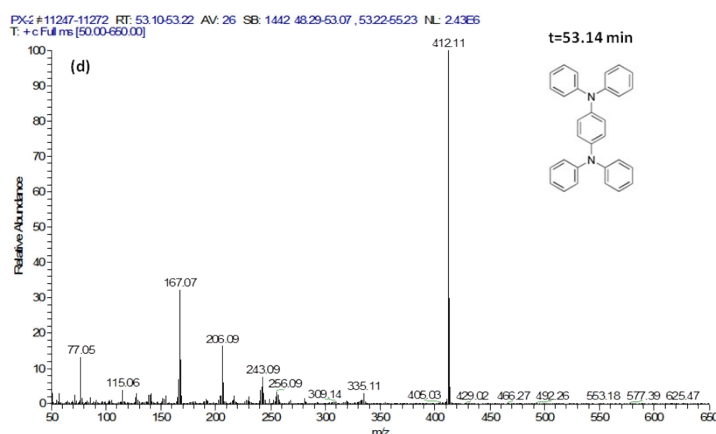


Fig. S1-4 Mass spectrum of the compound at 53.14 min.

MALDI-TOF-MS spectrometry is an efficient identification technique to analyze the molecular weight and the degree of polymerization of the polymers and here were utilized.²⁶ From MALDI-TOF-MS spectra of the as-prepared polymers in Fig. S2-1 and Fig. S2-2, we can acquire some information marked in the Tab. S1 and Tab. S2. For PTPA, the smallest and the biggest molecular weight of the polymers combined with ion are 731 and 3890 Da, corresponding of the polymerization degree changing from three to sixteen in the polymer. As to PFTP, the smallest and the biggest molecular weight of the polymers combined with ion are 745 and 2978 Da, in accord with the polymerization changing from one to four in PFTP. Above results indicate that the prepared polytriphenylamine-based derivatives are actually the oligomers and/or macromolecules, which limits the numbers of triphenylamine moieties in both PTPA and PFTP (FTP monomer can be defined as the integration of four triphenylamine moieties) not to exceed sixteen.

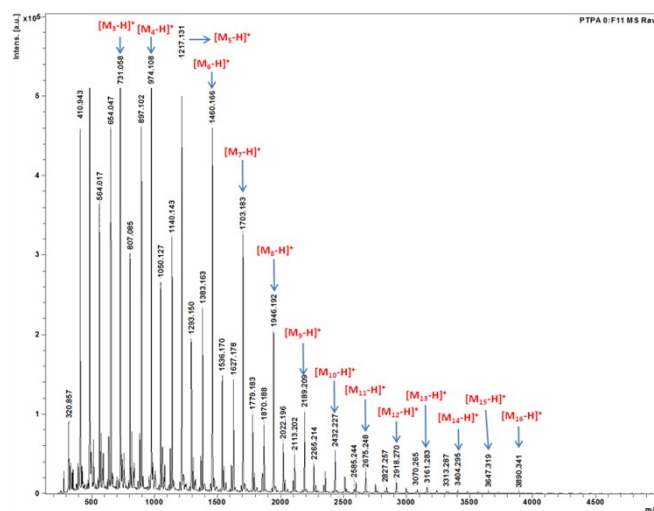


Fig. S2-1 MALDI-TOF-MS spectrum of PTPA.

Tab. S1 Analysis of MALDI-TOF-MS spectrum of PTPA.

$[M_n-H]^+$	Calculated	Found
n=3	730	731
n=4	973	974

n=5	1216	1217
n=6	1459	1460
n=7	1702	1703
n=8	1945	1946
n=9	2189	2189
n=10	2432	2432
n=11	2675	2675
n=12	2918	2918
n=13	3161	3161
n=14	3404	3404
n=15	3647	3647
n=16	3890	3890

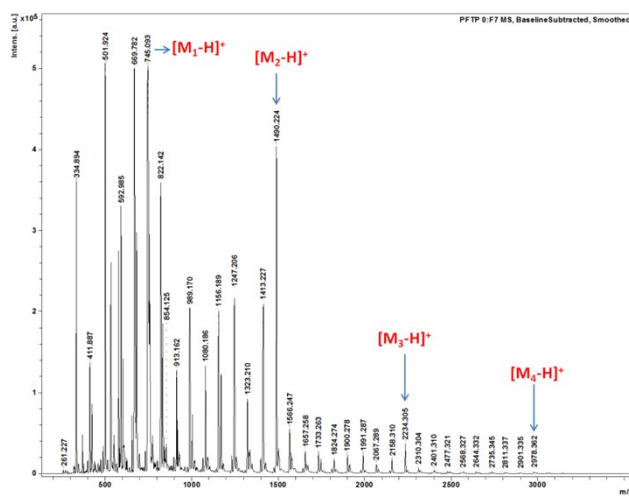


Fig. S2-2 MALDI-TOF-MS spectrum of PFTP.

Tab.S2 Analysis of MALDI-TOF-MS spectrum of PFTP.

$[M_n-H]^+$	Calculated	Found
n=1	745	745
n=2	1489	1490
n=3	2234	2234
n=4	2978	2978