

Multi-Component Post-Polymerization Modification Reactions of Polymers Featuring Lignin-Model Compounds

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SUPPORTING INFORMATION

Experimental Section

Synthesis of methacrylated vanillin (MV): In principle, the title compound was synthesized according to a previously reported method except for the purification process.¹ The obtained crude product was purified by recrystallization (CHCl₃/hexane), and the obtained white solid was dried under vacuum to produce a methacrylated vanillin (MV). The spectroscopic data of the obtained product gave a good agreement with reported values.¹ Yield: 14.3 g (66.0%).

¹H NMR (500 MHz, CDCl₃) δ: 9.95 (s, 1H), 7.54 – 7.41 (m, 2H), 7.29 – 7.20 (m, 1H), 6.40 – 6.37 (m, 1H), 5.81 – 5.78 (m, 1H), 3.89 (s, 3H), 2.09 – 2.05 (m, 3H).

Synthesis of methacrylated syringaldehyde (MS): Under N₂ atmosphere, syringaldehyde (20.0 g, 110 mmol, 1.0 eq.), DMAP (322 mg, 2.64 mmol, 2.4 mol %), CH₂Cl₂ (50 mL), and methacrylic anhydride (20.9 mL, 131.7 mmol, 1.2 eq.) were added to two-necked round-bottom flask and stirred for 3 hours at room temperature, after which the reaction mixture was allowed to be stirred for 48 hours at 45 °C. The resulting reaction product was diluted in CH₂Cl₂ and washed with 1N HCl aqueous solution, saturated NaHCO₃ aqueous solution, and water. After the solvent was evaporated, the crude product was purified by recrystallization (CHCl₃/hexane), and the obtained white solid was dried under vacuum to produce a methacrylated syringaldehyde (MS). The spectroscopic data of the obtained product gave a good agreement with reported values.² Yield: 15.0 g (54.4%).

¹H NMR (500 MHz, CDCl₃) δ: 9.92 (s, 1H), 7.17 (s, 2H), 6.42 – 6.40 (m, 1H), 5.83 – 5.73 (m, 1H), 3.90 (s, 6H), 2.09 (s, 3H).

References

1. Stanzione, J. F.; Sadler, J. M.; La Scala, J. J.; Wool, R. P., Lignin Model Compounds as Bio-Based Reactive Diluents for Liquid Molding Resins. *ChemSusChem* **2012**, *5* (7), 1291-1297.
2. Zhou, J.; Zhang, H.; Deng, J.; Wu, Y., High Glass-Transition Temperature Acrylate Polymers Derived from Biomasses, Syringaldehyde, and Vanillin. *Macromol. Chem. Phys.* **2016**, *217* (21), 2402-2408.

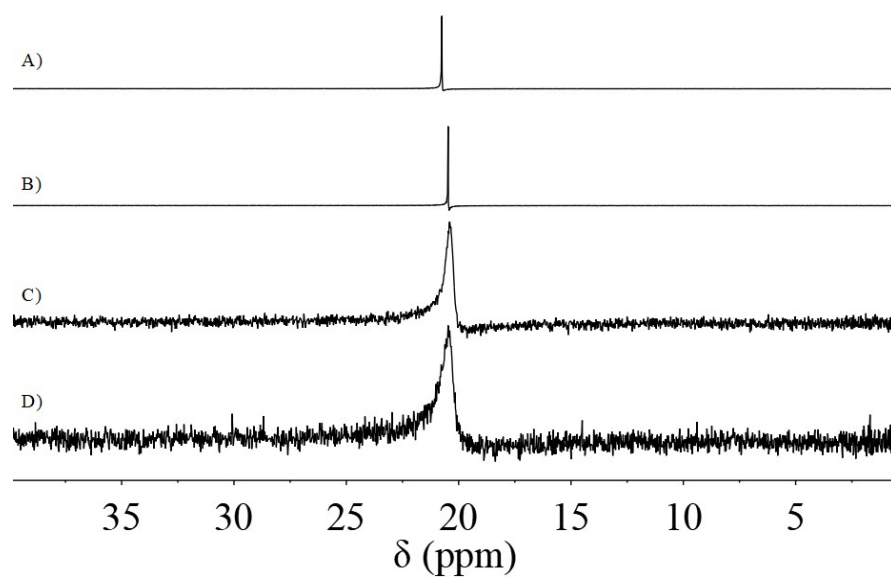


Fig. S1 ^{31}P NMR spectra of the model compounds (V-AP (A) and S-AP (B)) and the obtained polymers after Kabachnik-Fields reaction on PMV (C) (PMV-1, Table 1) and PMS (D) (PMS-1, Table 1) with *p*-anisidine and diisopropyl phosphite in CDCl_3 at 25 °C.

Waterfall plots for kinetic experiments

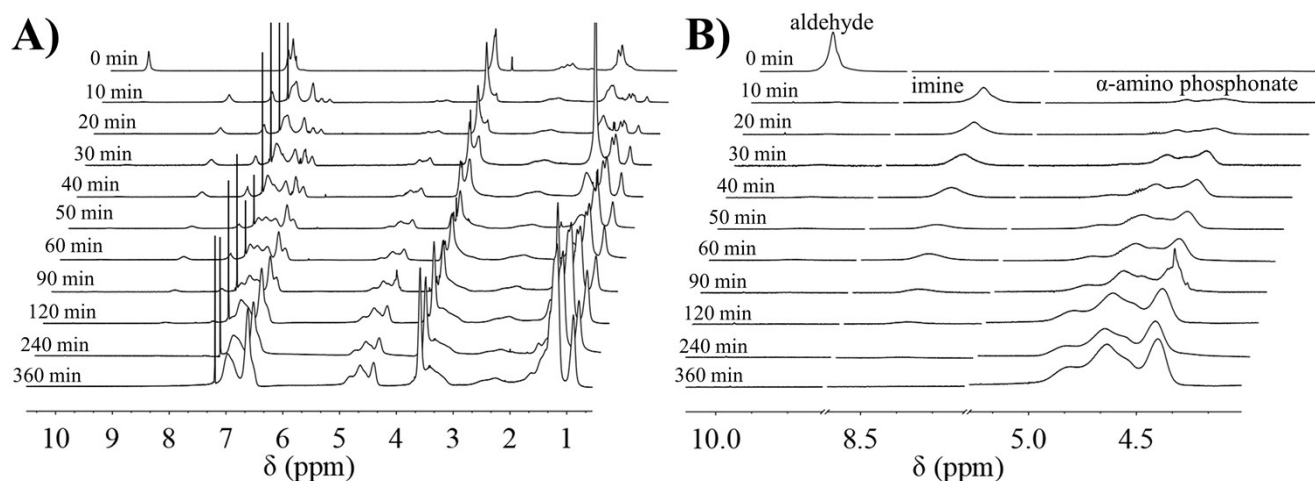


Fig. S2 Waterfall plots (A; whole regions and B; magnified regions) of the ¹H NMR spectra in CDCl₃ at 55 °C of the kinetic experiments for PMV with *p*-anisidine and diisopropyl phosphite. Reaction conditions are as follows: 1,4-dioxane as a solvent; initial aldehyde concentration was adjusted to 1.1 mol·L⁻¹; Ar atmosphere; [CHO]₀/[amine]₀/[phosphite]₀ was adjusted to 1/1.1/1.5.

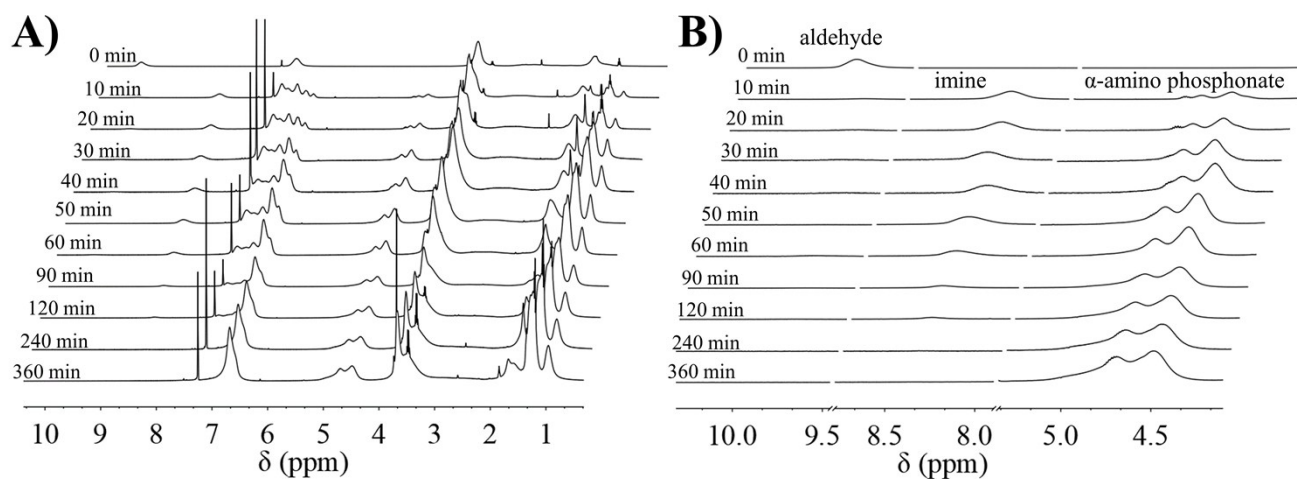


Fig. S3 Waterfall plots (A; whole regions and B; magnified regions) of the ¹H NMR spectra in CDCl₃ at 55 °C of the kinetic experiments for PMS with *p*-anisidine and diisopropyl phosphite. Reaction conditions are as follows: 1,4-dioxane as a solvent; initial aldehyde concentration was adjusted to 1.1 mol·L⁻¹; Ar atmosphere; [CHO]₀/[amine]₀/[phosphite]₀ was adjusted to 1/1.1/1.5.

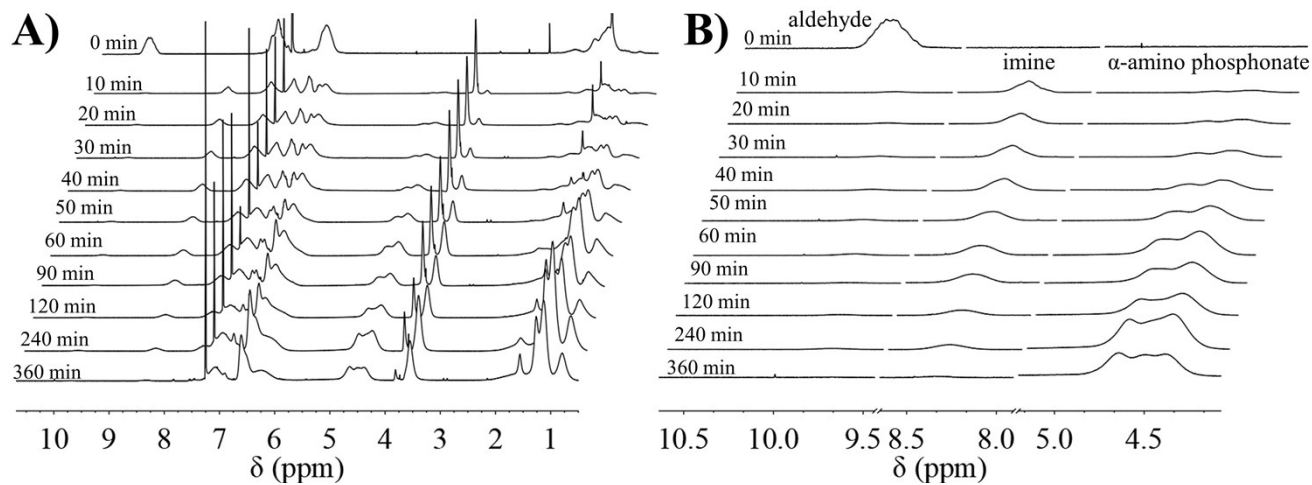


Fig. S4 Waterfall plots (A; whole regions and B; magnified regions) of the ^1H NMR spectra in CDCl_3 at 55°C of the kinetic experiments for poly(St-CHO) with *p*-anisidine and diisopropyl phosphite. Reaction conditions are as follows: 1,4-dioxane as a solvent; initial aldehyde concentration was adjusted to $1.1\text{ mol}\cdot\text{L}^{-1}$; Ar atmosphere; $[\text{CHO}]_0/[\text{amine}]_0/[\text{phosphite}]_0$ was adjusted to 1/1.1/1.5.

Structural Proofs for obtained polymers

(¹H NMR spectra for PMVs)

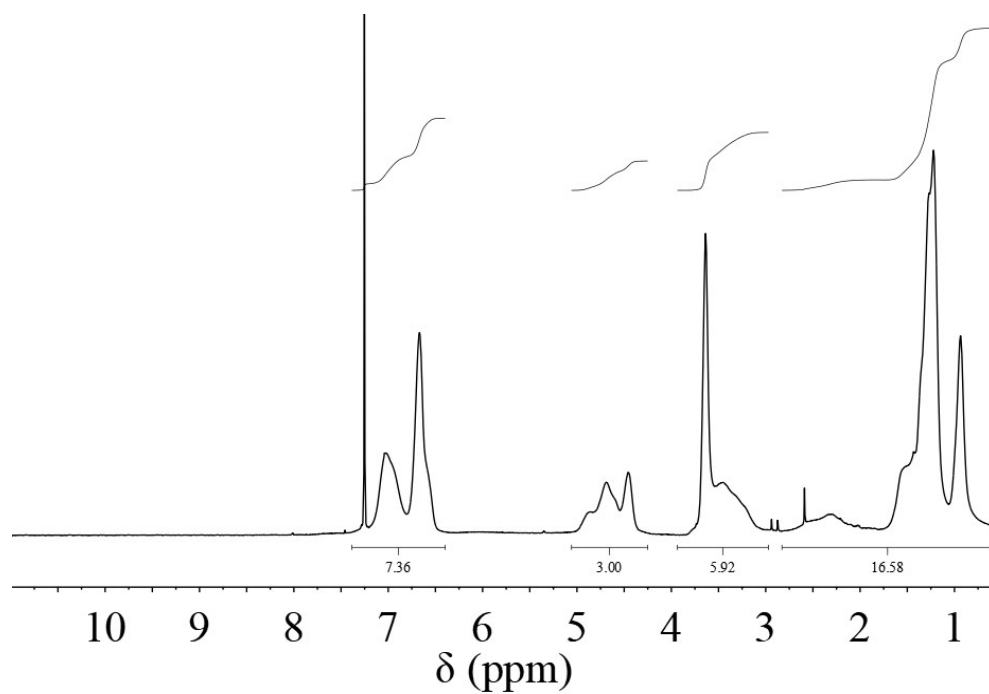


Fig. S5 ¹H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMV with *p*-anisidine and diisopropyl phosphite (PMV-1, Table 1) in CDCl₃ at 55 °C.

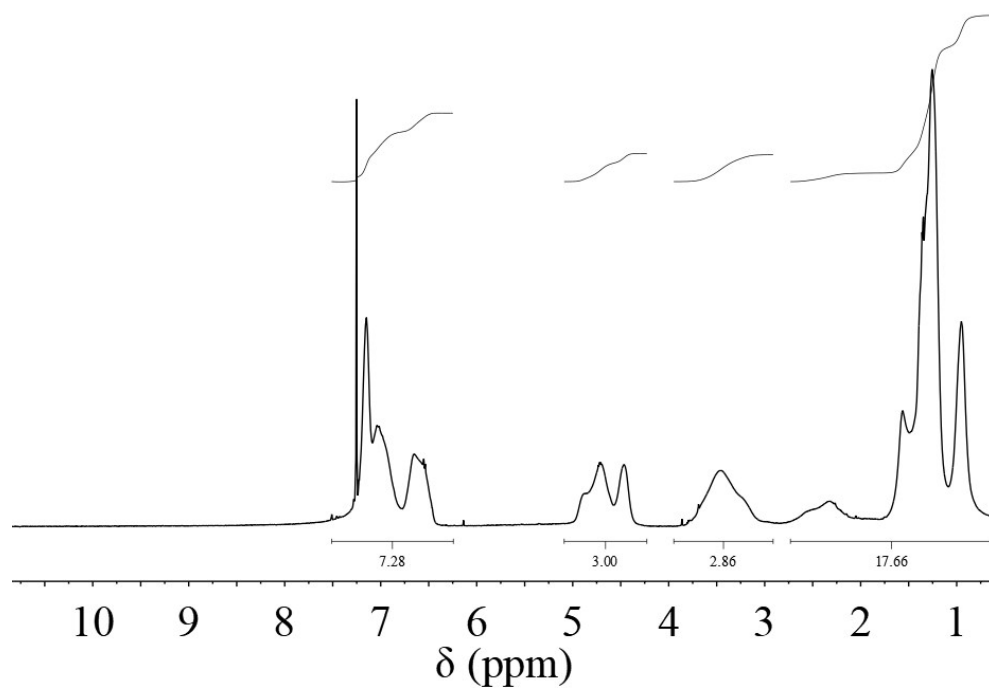


Fig. S6 ¹H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMV with *p*-bromoaniline and diisopropyl phosphite (PMV-2, Table 1) in CDCl₃ at 55 °C.

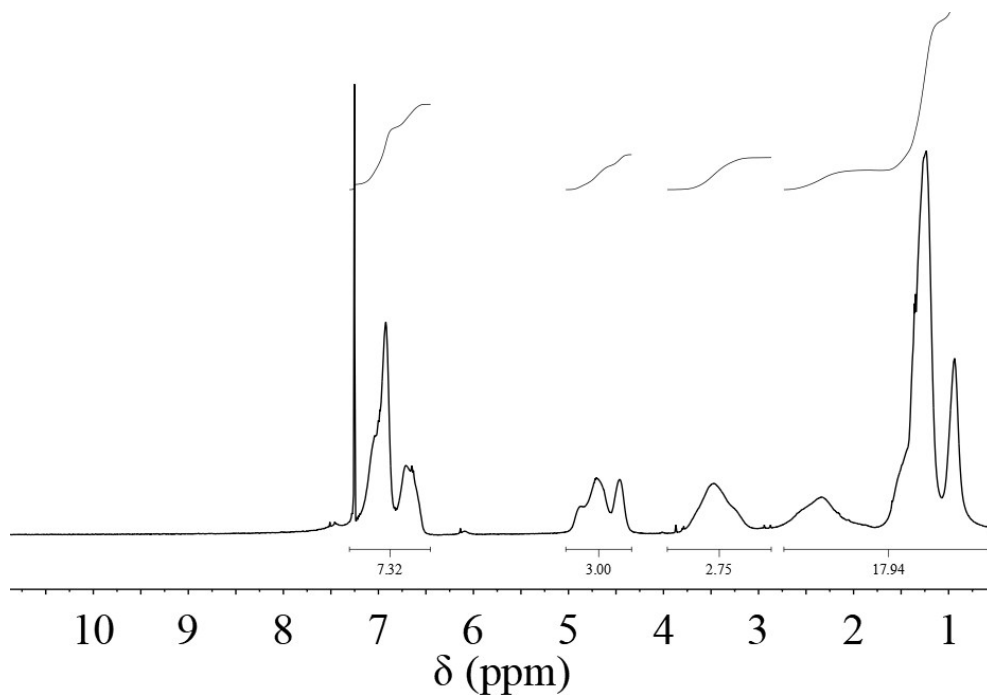


Fig. S7 ¹H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMV with 4-(trifluoromethoxy)aniline and diisopropyl phosphite (PMV-3, Table 1) in CDCl₃ at 55 °C.

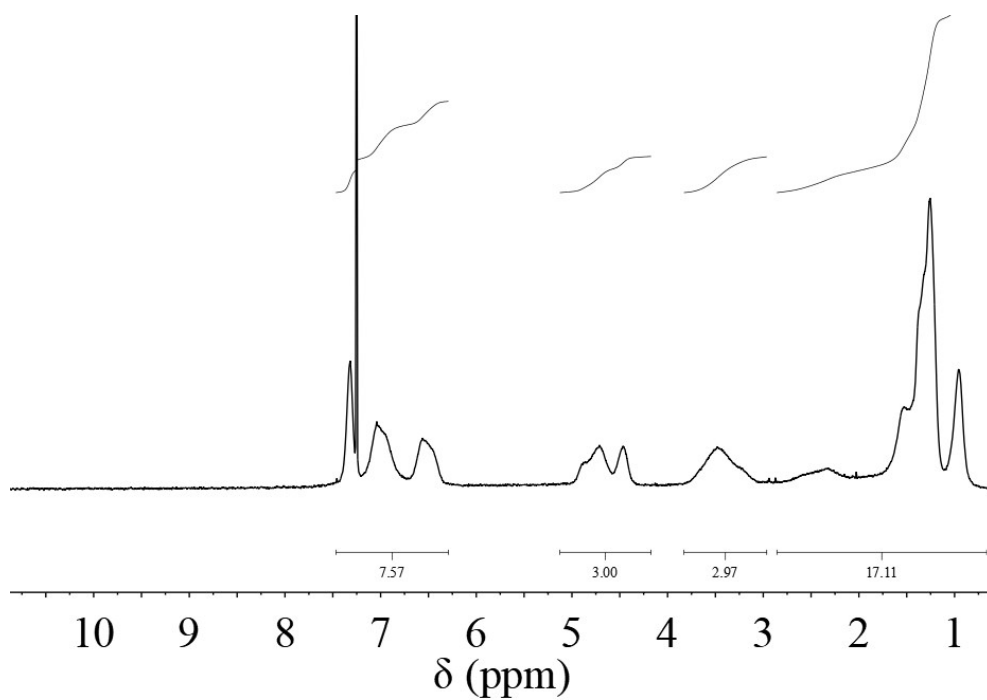


Fig. S8 ¹H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMV with *p*-Iodoaniline and diisobutyl phosphite (PMV-4, Table 1) in CDCl₃ at 55 °C.

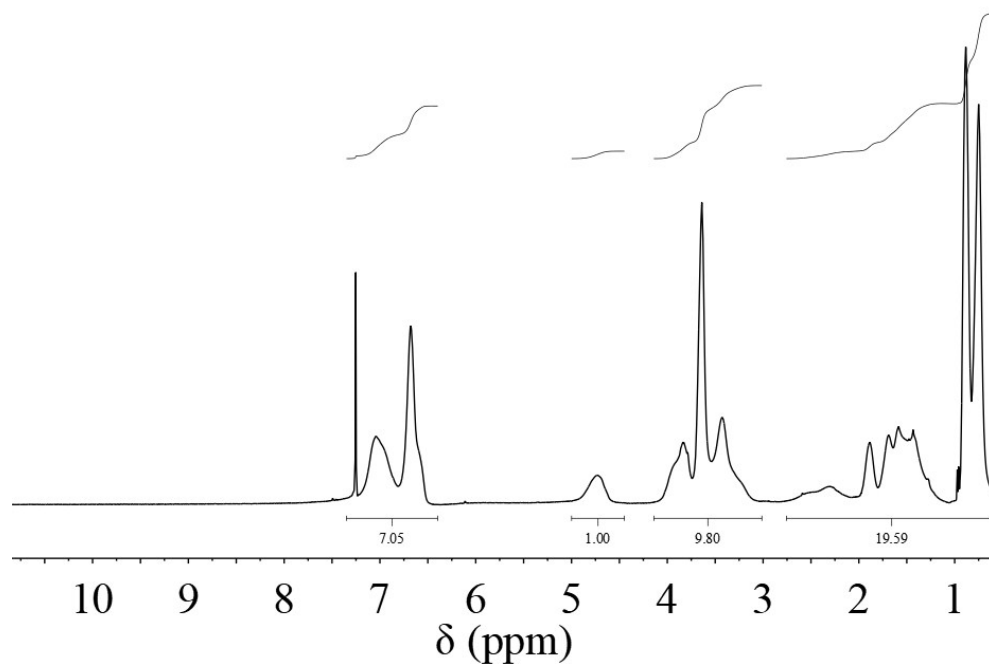


Fig. S9 ¹H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMV with *p*-anisidine and diisobutyl phosphite (PMV-5, Table 1) in CDCl₃ at 55 °C.

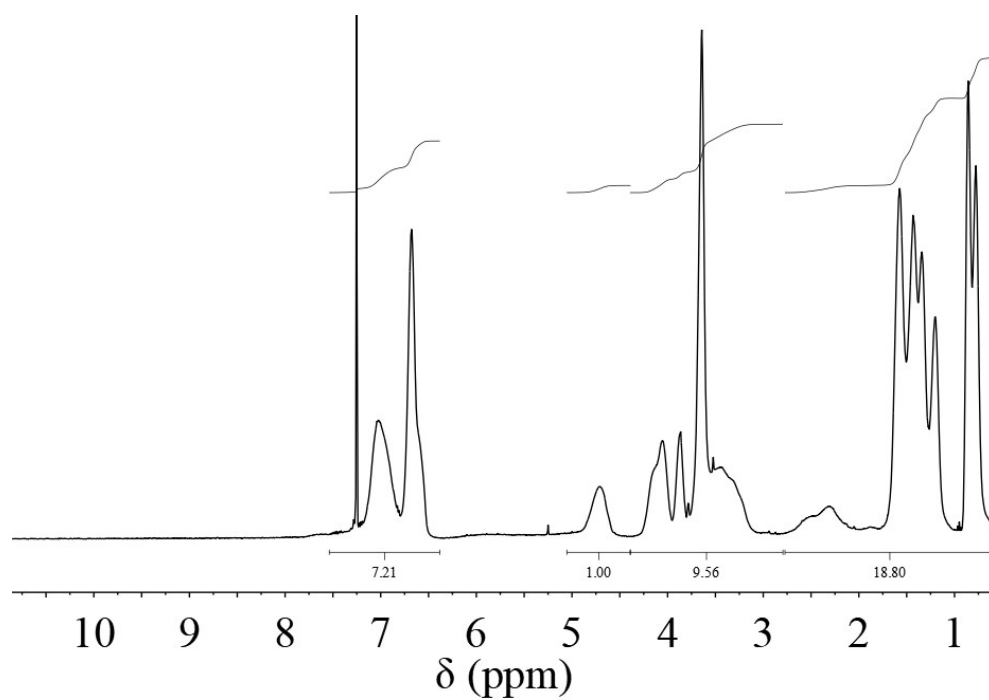


Fig. S10 ¹H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMV with *p*-anisidine and dibutyl phosphite (PMV-6, Table 1) in CDCl₃ at 55 °C.

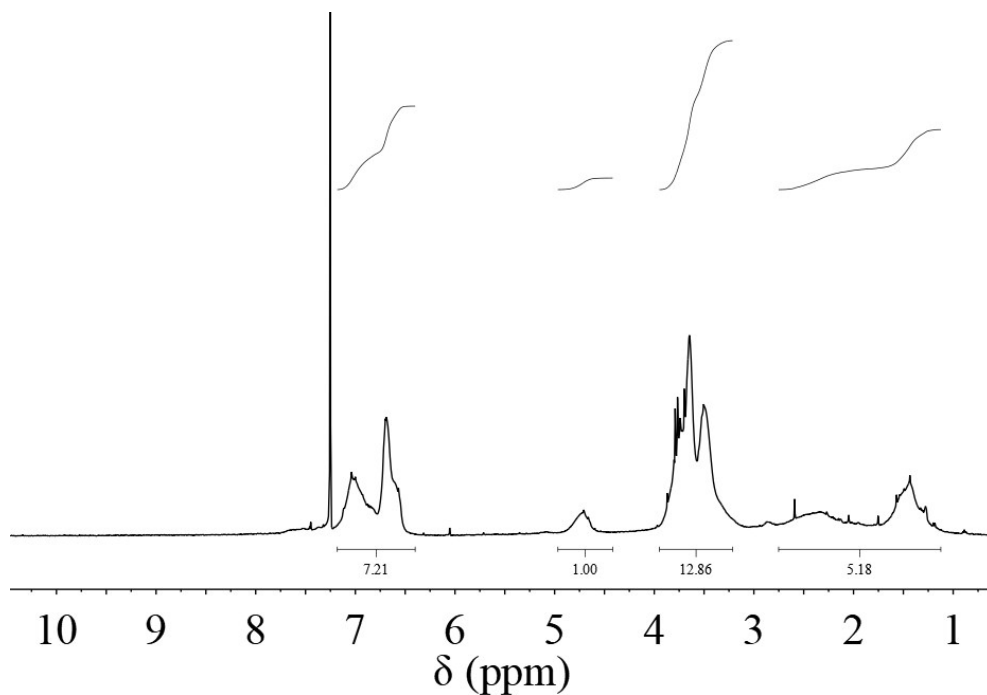


Fig. S11 ^1H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMV with *p*-anisidine and dimethyl phosphite (PMV-7, Table 1) in CDCl_3 at 55 $^\circ\text{C}$.

(^1H NMR for spectra PMSs)

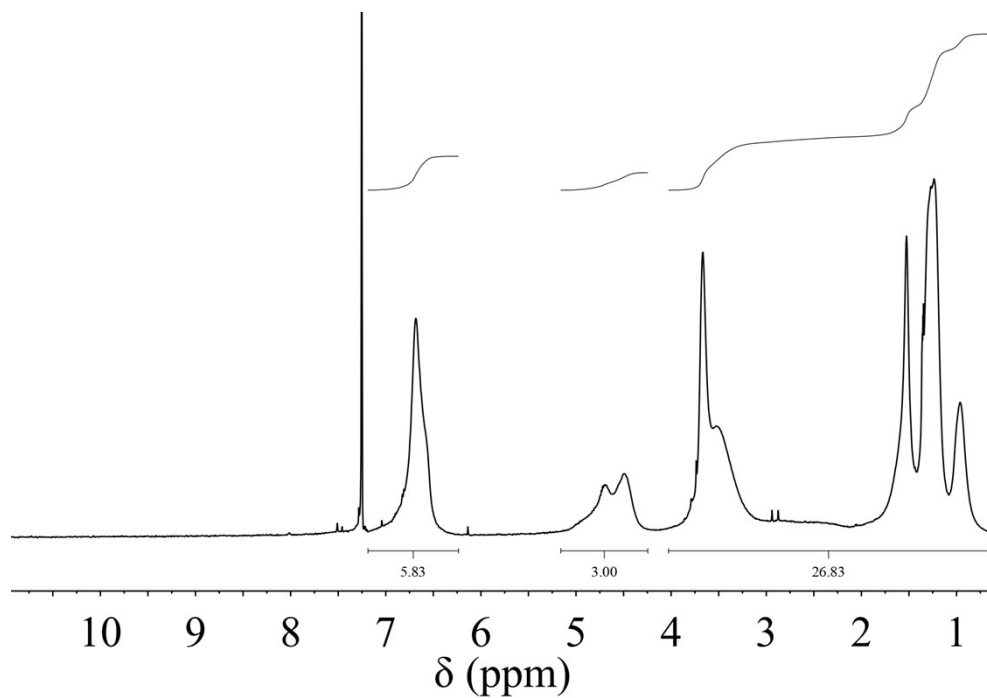


Fig. S12 ^1H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMS with *p*-anisidine and diisopropyl phosphite (PMS-1, Table 1) in CDCl_3 at 55 $^\circ\text{C}$.

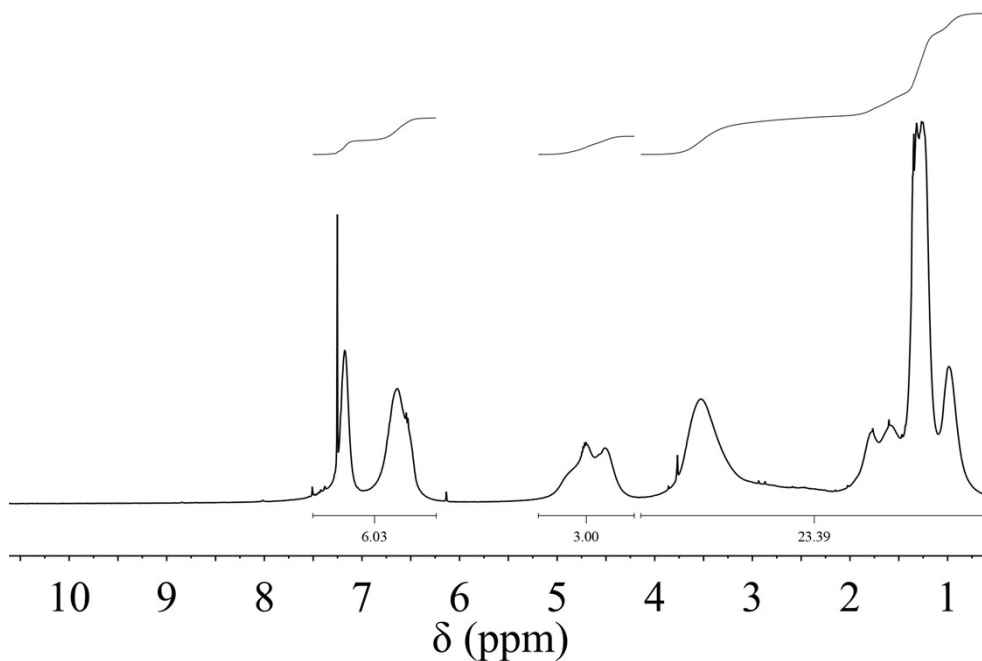


Fig. S13 ¹H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMS with *p*-bromoaniline and diisopropyl phosphite (PMS-2, Table 1) in CDCl₃ at 55 °C.

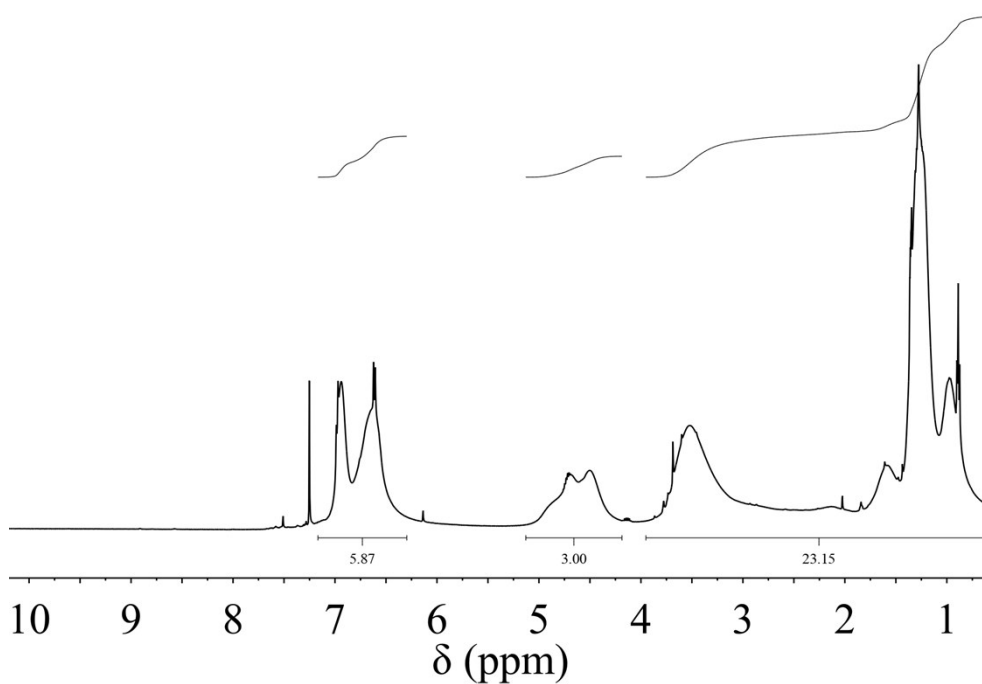


Fig. S14 ¹H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMS with 4-(trifluoromethoxy)aniline and diisopropyl phosphite (PMS-3, Table 1) in CDCl₃ at 55 °C.

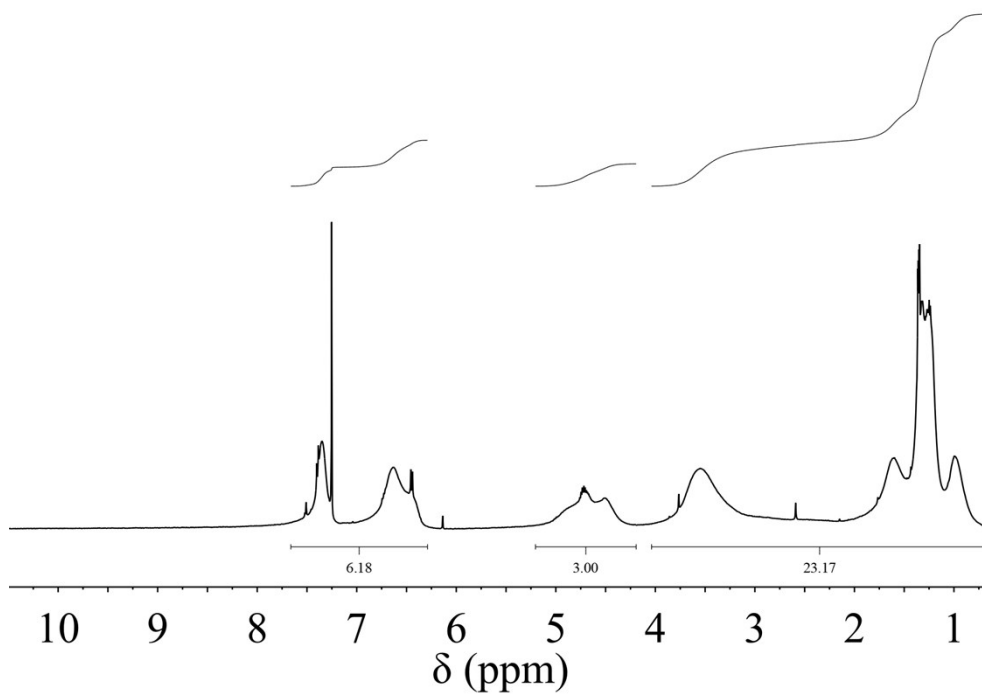


Fig. S15 ¹H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMS with 4-iodo aniline and diisopropyl phosphite (PMS-4, Table 1) in CDCl₃ at 55 °C.

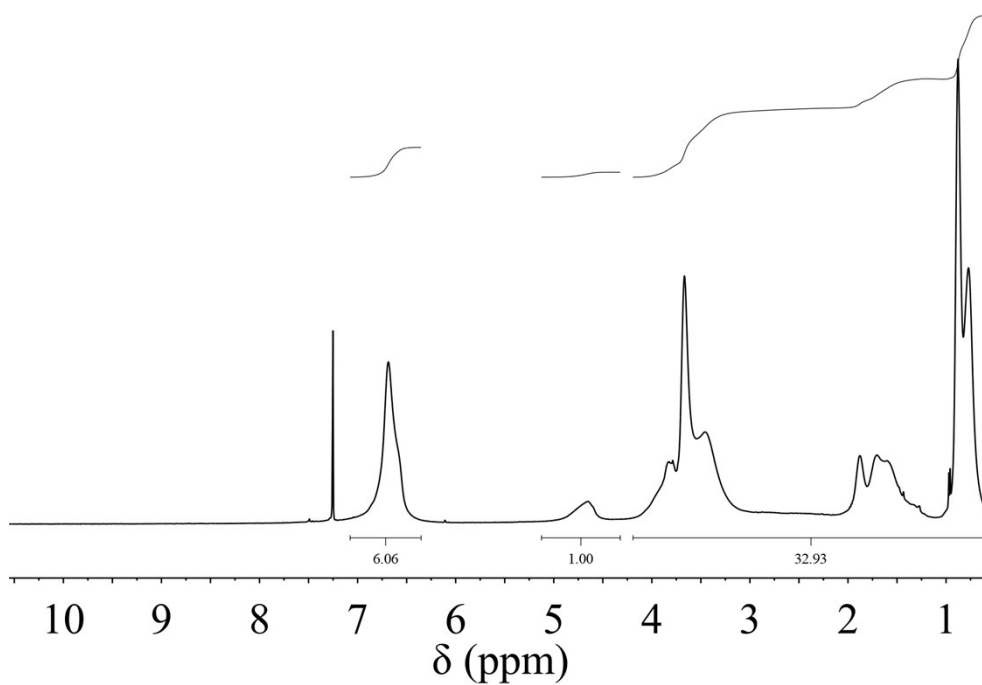


Fig. S16 ¹H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMS with *p*-anisidine and diisobutyl phosphite (PMS-5, Table 1) in CDCl₃ at 55 °C.

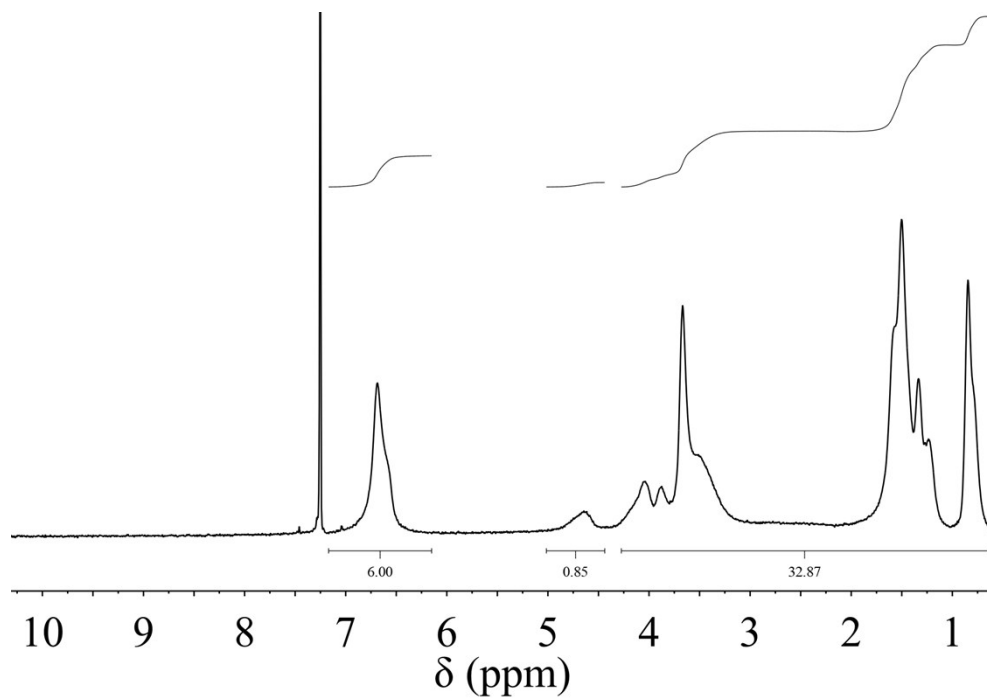


Fig. S17 ^1H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMS with *p*-anisidine and dibutyl phosphite (PMS-6, Table 1) in CDCl_3 at 55 $^\circ\text{C}$.

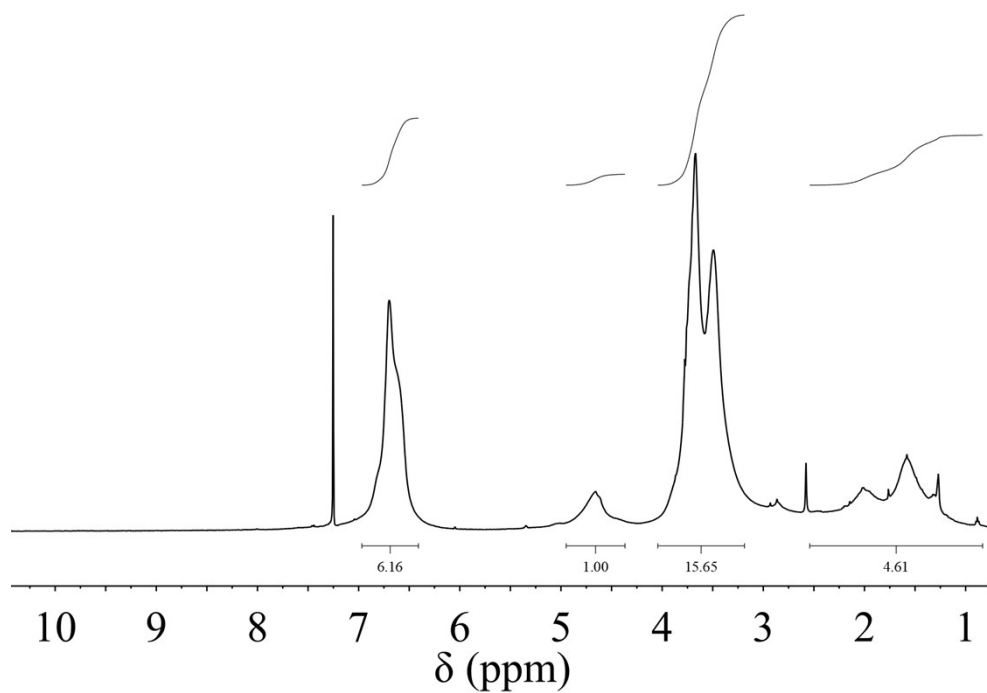


Fig. S18 ^1H NMR spectrum of the obtained polymer after Kabachnik-Fields reaction on PMS with *p*-anisidine and dimethyl phosphite (PMS-7, Table 1) in CDCl_3 at 55 $^\circ\text{C}$.

(³¹P NMR spectra for PMV and PMS derived samples)

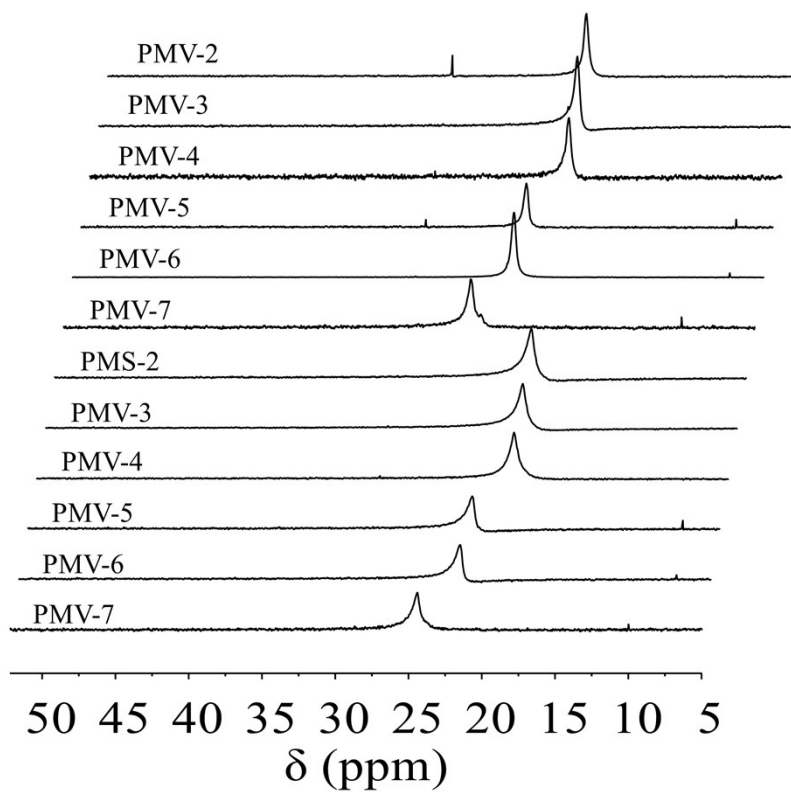


Fig. S19 ³¹P NMR spectra of all the polymeric amino phosphonate esters synthesized via KF-PMR of PMV and PMS in CDCl₃.

(SEC analysis of all the obtained polymers)

Table S1. Molecular weights and dispersity of all the polymer samples determined based on polystyrene standards

sample	M_n ($10^3 \text{ kg} \cdot \text{mol}^{-1}$)	M_w ($10^3 \text{ kg} \cdot \text{mol}^{-1}$)	\bar{D}
PMV ^a	14	70	5.0
PMV-1 ^a	32	74	2.3
PMV-2 ^a	18	60	3.3
PMV-3 ^a	16	58	3.6
PMV-4 ^b	38	225	5.9
PMV-5 ^b	31	197	6.3
PMV-6 ^b	30	248	8.1
PMV-7 ^b	23	119	5.1
PMS ^a	13	35	2.7
PMS-1 ^a	18	47	2.6
PMS-2 ^a	18	51	2.8
PMS-3 ^a	29	81	2.8
PMS-4 ^a	24	65	2.7
PMS-5 ^b	28	97	3.5
PMS-6 ^b	28	99	3.6
PMS-7 ^b	13	57	4.3

^a Measured in CHCl_3 at r.t. at a flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$ by JASCO GPC system comprised of PU-2080 Plus, UV-2077 plus, DG-980-50, and RI-2031 Plus (JASCO Co., Tokyo, Japan) equipped with TSKgel MultiporeH_{XL}-M (Tosoh Co., Tokyo, Japan). ^b Measured in DMF containing $0.01 \text{ mol} \cdot \text{L}^{-1}$ LiBr at $40 \text{ }^\circ\text{C}$ at a flow rate of $1.0 \text{ mL} \cdot \text{min}^{-1}$ by Prominence UFLC system (Shimadzu Co., Kyoto, Japan) equipped with TSK gel α -M (Tosoh Co., Tokyo, Japan).

(DSC curves for PMV and PMS derived samples)

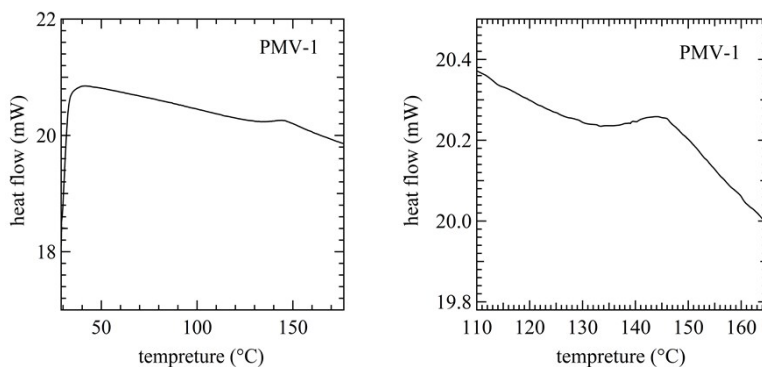


Fig. S20 DSC curves (left; whole region, right; magnified region) of the obtained polymer after Kabachnik-Fields reaction on PMV with *p*-anisidine and diisopropyl phosphite (PMV-1, Table 1).

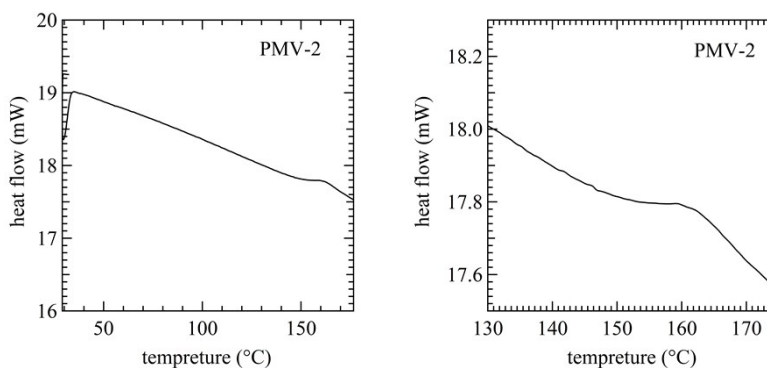


Fig. S21 DSC curves (left; whole region, right; magnified region) of the obtained polymer after Kabachnik-Fields reaction on PMV with *p*-bromoaniline and diisopropyl phosphite (PMV-2, Table 1).

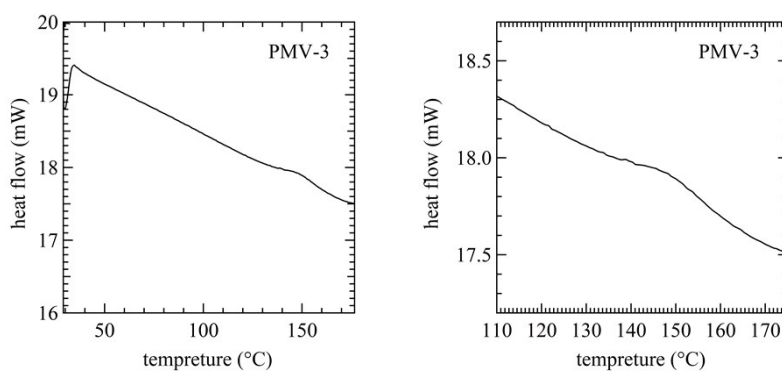


Fig. S22 DSC curves (left; whole region, right; magnified region) of the obtained polymer after Kabachnik-Fields reaction on PMV with 4-(trifluoromethoxy)aniline and diisopropyl phosphite (PMV-3, Table 1).

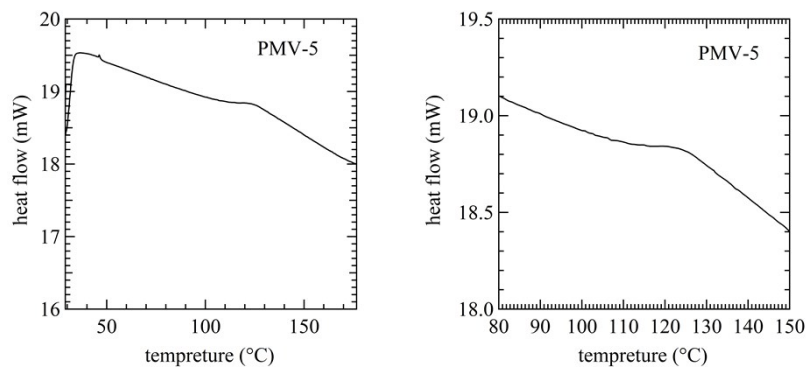


Fig. S23 DSC curves (left; whole region, right; magnified region) of the obtained polymer after Kabachnik-Fields reaction on PMV with *p*-anisidine and diisobutyl phosphite (PMV-5, Table 1).

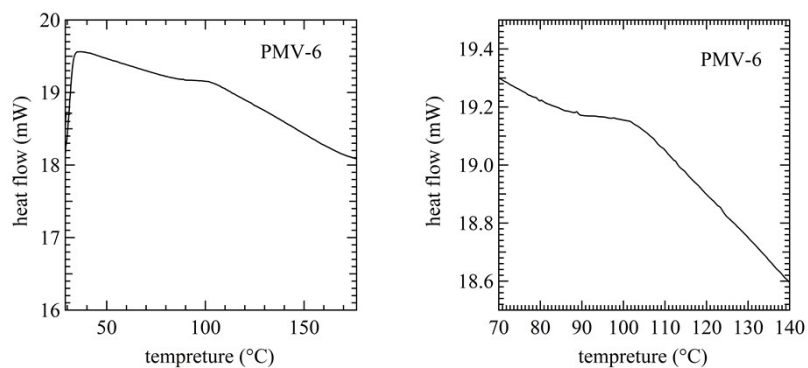


Fig. S24 DSC curves (left; whole region, right; magnified region) of the obtained polymer after Kabachnik-Fields reaction on PMV with *p*-anisidine and dibutyl phosphite (PMV-6, Table 1).

(The magnified DTA profiles for PMV and PMS derived samples)

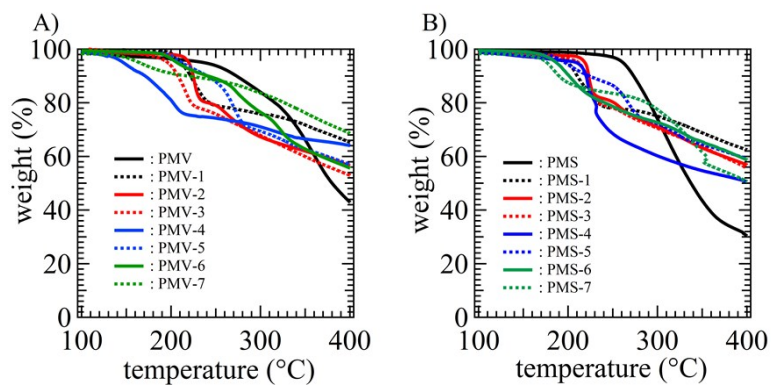


Fig. S25 TG/DTA curves in the range from 100 to 400 °C for the obtained polymers before and after the KF-PMR of PMV (A) and PMS (B) with aromatic amines and phosphites (the run numbers correspond to those in Table 1) measured at the heating rate of 10 °C·min⁻¹ in air.