Electronic Supplementary Information (ESI)

Coordination-insertion polymerization of polar allylbenzene monomers

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**General Procedures and Materials:** All syntheses involving air- and moisture sensitive compounds were carried out using standard Schlenk-type glassware (or in a glove box) under an atmosphere of nitrogen. All solvents were purified from the MBraun SPS system. NMR spectra for monomers and polymers were recorded on a Bruker AV400 (\(\text{^1H}: 400 \text{ MHz}, \text{^13C}: 100 \text{ MHz}\)) or a Bruker AV500 (\(\text{^1H}: 500 \text{ MHz}, \text{^13C}: 125 \text{ MHz}\)). NMR assignments were confirmed by \(\text{^1H}−\text{^1H} \text{COSY}, \text{^1H}−\text{^13C} \text{HSQC and } \text{^1H}−\text{^13C} \text{HMBC experiments when necessary. The molecular weights } (M_n) \text{ and molecular weight distributions } (M_w/M_n) \text{ of copolymers were measured by means of gel permeation chromatography (GPC) on a PL-GPC 220-type high-temperature chromatograph equipped with three PL-gel 10 μm Mixed-B LS type columns at 150 °C. Melting points } (T_m) \text{ of copolymers were measured through DSC analyses, which were carried out on a Q 100 DSC from TA Instruments under a nitrogen atmosphere at heating and cooling rates of 10 °C/min (temperature range: 20–180 °C).}

**Materials:**

\[(2,6-\text{PrC}_6\text{H}_3\text{NC(Me)C(Me)N}-2,6-\text{PrC}_6\text{H}_3)\text{Pd(CH}_3)(\text{Cl})\]¹, \(\text{Pd}(\text{C}_6\text{H}_9\text{OCH}_3)_2\text{C}_6\text{H}_4\text{SO}_3)(\text{CH}_3)(\text{DMSO})², \(\text{Pd}(\text{C}_6\text{H}_{11})_2\text{C}_6\text{H}_4\text{SO}_3)(\text{CH}_3)(\text{SO(CH}_3)_2)³, \text{2-methoxy allylbenzene}⁴, \text{2-acetoxy allylbenzene}⁵, \text{2-allylbenzaldehyde}⁶, \text{2-allylbromobenzene}⁶ \text{ and } \text{2-(N,N-dimethylamino) allylbenzene}⁷ \text{ were prepared according to the literature procedures. All other reagents were commercially available and used as received.}
A general procedure for the copolymerization of polar monomer with ethylene.

In a typical experiment, a 150 mL glass pressure reactor connected with a high pressure gas line was firstly dried at 90 °C under vacuum for at least 1 h. The glass reactor was then adjusted to the desired polymerization temperature. 23 mL of toluene and the desired polar allylbenzene monomer were added to the reactor under N₂ atmosphere, then the desired amount of Pd(II) catalyst in 2 mL of CH₂Cl₂ was injected into the polymerization system via syringe subsequently. With a rapid stirring, the reactor was pressurized and maintained at the desired pressure of ethylene. After 1 h, the pressure reactor was vented and the copolymer was precipitated in ethanol, filtered and dried at 50 °C for at least 24 h under vacuum.
Figure S1. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of 2-methoxy allylbenzene.

Figure S2. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of 2-acetoxy allylbenzene.
Figure S3. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of 2-allylbenzaldehyde.

Figure S4. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of 2-allylbromobenzene.
Figure S5. $^1$H NMR spectrum (500 MHz, 298 K, CDCl$_3$) of 2-(N,N-dimethylamino) allylbenzene.
Figure S6. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 4.

Figure S7. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 5.
Figure S8. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 5.

Figure S9. $^1$H-$^1$H COSY NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 5.
Figure S10. $^1$H-$^{13}$C HSQC NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 5.

Figure S11. $^1$H-$^{13}$C HMBC NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 5.
Figure S12. $^1$H NMR spectrum (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C) of the copolymer from table 1, entry 6.

Figure S13. $^1$H NMR spectrum (400 MHz, $\text{C}_2\text{D}_2\text{Cl}_4$, 110 °C) of the copolymer from table 1, entry 7.
**Figure S14.** $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 7.

**Figure S15.** $^1$H-$^1$H COSY NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 7.
Figure S16. $^1$H-$^{13}$C HSQC NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 7.

Figure S17. $^1$H-$^{13}$C HMBC NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 7.
Figure S18. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 8.

Figure S19. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 9.
Figure S20. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 9.

Figure S21. $^1$H-$^1$H COSY NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 9.
Figure S22. $^1$H-$^{13}$C HSQC NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 9.

Figure S23. $^1$H-$^{13}$C HMBC NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 9.
Figure S24. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 10.

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Figure S28. $^1$H-$^1$C HSQC NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 11.

Figure S29. $^1$H-$^1$C HMBC NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 11.
Figure S30. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 12.

Figure S31. $^1$H NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 13.
Figure S32. $^{13}$C NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 13.

Figure S33. $^1$H–$^1$H COSY NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 13.
Figure S34. $^1$H-$^{13}$C HSQC NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 13.

Figure S35. $^1$H-$^{13}$C HMBC NMR spectrum (400 MHz, C$_2$D$_2$Cl$_4$, 110 °C) of the copolymer from table 1, entry 13.
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References