Supporting Information

Synthesis of self-healing polymers by scandium-catalyzed copolymerization of ethylene and anisylpropylenes

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1. Materials and Methods

All manipulations of air and moisture-sensitive compounds were performed under a dry nitrogen atmosphere by use of standard Schlenk techniques or a nitrogen-filled Mbraun glovebox. Nitrogen was purified by being passed through a Dryclean column DC-A4 (4 Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-XR column (Nikka Seiko Co.). Solvents were purified by an Mbraun SPS-800 Solvent Purification System and dried over fresh Na chips in the glovebox. [Ph₃C][B(C₆F₅)₄] (97%) was purchased from Strem Chemical Corporation and used without purification. Rare-earth catalysts Cp′Sc(CH₂C₆H₄NMe₂-o)₂ (Cp′ = C₅H₅ and C₅Me₄SiMe₃), were synthesized according to the literatures. 3-(2-anisyl)-1-propylene (AP) was purchased from Wako Pure Chemical Industries Ltd. and purified by distillation from Al(octyl)₃ (25 wt.% in hexanes) before use.

The deuterated solvents benzene-d₆ (99.6 atom % D), CDCl₃ (99.8 atom % D), and 1,1,2,2-tetrachloroethane-d₂ (99.6 atom % D) were obtained from Kanto Chemical Co. Inc. and Cambridge Isotope. The NMR data of the polymers were obtained on a Bruker AVANCE III HD 500 NMR (FT, 500 MHz for ¹H; 125 MHz for ¹³C{¹H}) spectrometer with CDCl₃ (at 26.8 °C) or 1,1,2,2-C₂D₂Cl₄ (at 26.8 °C or 120 °C) as a solvent. The chemical shifts for ¹H NMR were recorded in ppm downfield from tetramethylsilane (TMS) with the solvent resonance as the internal standard (7.16 ppm for C₆D₆, 7.26 ppm for CDCl₃, 6.0 ppm for 1,1,2,2-C₂D₂Cl₄). The chemical shifts for ¹³C{¹H} NMR were recorded in ppm downfield using the central peak of C₆D₆ (128.06 ppm) CDCl₃ (77.16 ppm), 1,1,2,2-C₂D₂Cl₄ (73.78 ppm) as the internal standard. Coupling constants (J) are reported in Hz and refer to apparent peak multiplications. The abbreviations s, d, t, q and m stand for singlet, doublet, triplet, quartet and multiplet in that order.

The molecular weights and the molecular weight distributions of homopolymers were determined at 40 °C by gel permeation chromatography (GPC) on a HLC-8320 GPC apparatus (Tosoh Corporation). THF was employed as an eluent at a flow rate of 0.35 mL/min. The molecular weights and the molecular weight distributions of all the copolymers were determined at 145 °C by high temperature gel permeation chromatography (HT-GPC) on a HLC-8321GPC/HT apparatus (Tosoh Corporation). 1,2-Dichlorobenzene (DCB) was employed as an eluent at a flow rate of 1.0 mL/min. The
calibration was made by use of polystyrene standard (Tosoh Corporation). The DSC measurements were performed on a DSC 6220 (SII Corporation) at a rate of 10 °C/min. Any thermal history difference in the polymers was eliminated by first heating the specimen to 150 °C (or 200 °C), cooling at 10 °C/min to −100 °C (or −30 °C) and then recording the second DSC scan. Transmittance of copolymer film with 0.5 mm thickness was measured on a UV-2400 UV-VIS recording spectrophotometer (Shimadzu) in the range of 400 nm to 900 nm. The self-healing videos were recorded on a KEYENCE model VHX-5000 digital microscope. Wide-angle X-ray diffraction (WAXD) and small-angle X-ray scattering (SAXS) measurements were performed at BL05XU beam line of SPring-8 (Japan Synchrotron Radiation Research Institute, Hyogo, Japan). The X-ray wavelength was set at 0.1 nm. The 2D WAXD and 2D SAXS patterns were recorded by a 941 × 1043 pixel PILATUS 1M with a pixel size of 172 × 172 μm² (DECTRIS, Switzerland) as the X-ray detector. The distances from the sample to the detector were 106 mm for WAXD and 3906 mm for SAXS. The measurements were performed under precise temperature control by using sample chamber equipped with a block heater. The scattering vector was defined as \( q = \left( \frac{4\pi}{\lambda} \right) \sin \theta \), where \( 2\theta \) is the scattering angle. The scattering vector was calibrated using the peak position of CeO₂ for WAXD and collagen for SAXS. TGA was recorded on EXSTAR TG/DTA-6200 thermo balance (Hitachi High-Tech Science Corporation, Tokyo, Japan). The temperature range is 40 to 600 °C at the heating rate of 10 °C min⁻¹. TEM measurement was performed on a JEOL model JEM-2100F/SP operated at 200-kV accelerating voltage. Ultrathin film of P5 has been prepared by solvent volatilization of dilute P5 solution in CH₂Cl₂ (0.5 mg/mL) on a 400-mesh carbon-coated copper grid.

2. General procedure for the homopolymerization of 3-(2-anisyl)-1-propylene (AP)

Polymerization of AP (Table S1, run 1): In a THF-free glovebox, a toluene solution (0.5 mL) of [Ph₃C][B(C₆F₅)₄] (9.2 mg, 0.01 mmol) was slowly added to a toluene solution (0.5 mL) of C₅H₅Sc(CH₂C₆H₄NMe₂-o)₂ (I, 3.8 mg, 0.01 mmol) under magnetic stirring in a 10 mL glass tube with cap. After the mixture was stirred for 5 min, AP (148.0 mg, 1.0 mmol, 0.5 M in toluene) was added into the reaction solution. The tube was sealed and kept stirring in the glovebox at room temperature for 12 mins. The
polymerization was quenched by addition of methanol (10 mL). Then the mixture was poured into methanol (50 mL) to precipitate the polymer product. The precipitated polymer was dried under vacuum at 60 °C to a constant weight (148 mg, 100% yield).

Table S1. Homopolymerization of AP using scandium catalysts. 

| Run | [Sc] | [O]/[Sc] | Time | Yield (g) | $M_n$ ($10^3$ g mol$^{-1}$) | $M_w/M_n$ | $T_g^d$ | $T_m^d$ | $rrrr$ (%) 
|-----|------|---------|------|----------|----------------|-----------|-------|-------|---------| 
| 1 | 1 | 100/1 | 12 min | 0.15 | 13.7 | 1.62 | 67 | 152 | >99 | 
| 2$^f$ | 1 | 1000/1 | 1 h | 2.90 | 23.4 | 1.85 | 64 | 155 | >99 | 
| 3$^g$ | 1 | 1000/1 | 13 h | 2.96 | 4.65 | 2.20 | 63 | 158 | >99 | 
| 4 | 2 | 100/1 | 24 h | trace | - | - | - | - | - | 

$^a$ Conditions: [Sc] (0.01 mmol), [Ph$_3$C][B(C$_6$F$_5$)$_4$] (0.01 mmol), 3 mL toluene, 20 °C. $^b$ Yield of final polymer. $^c$ Determined by GPC in THF at 40 °C against polystyrene standard. $^d$ Determined by differential scanning calorimetry. $^e$ Determined by $^{13}$C-$^1$H NMR analysis. $^f$ 10 mL toluene. $^g$ 10 mL toluene, –20 °C.

At first, we examined the homo-polymerization of the commercially available 3-(2-anisyl)-1-propylene (AP) by using the C$_5$H$_5$-ligated scandium complex (C$_5$H$_5$)Sc(CH$_2$C$_6$H$_4$NMe$_2$-o)$_2$ (1) (Table S1). In combination with one equimolar amount of [Ph$_3$C][B(C$_6$F$_5$)$_4$] as a co-catalyst, complex 1 showed high activity and high stereoselectivity for the polymerization of AP at room temperature in toluene, quantitatively converting up to 1000 equimolar amounts of AP to the corresponding syndiotactic polymers ($rrrr > 99\%$) in 1 hour (Table S1, runs 1 and 2). The resulting polymer products were semi-crystalline materials, showing melting point ($T_m$) at 152-158 °C. The methoxy-free analogue, allylbenzene, did not give a polymer product under the same conditions. These results clearly demonstrate that the methoxy group in AP played a significantly important role in the present polymerization. In contrast with the high activity of 1, the sterically demanding C$_5$Me$_4$SiMe$_3$-ligated scandium analogue (C$_5$Me$_4$SiMe$_3$)Sc(CH$_2$C$_6$H$_4$NMe$_2$-o)$_2$ (2) was much less effective for the polymerization of AP, affording only a trace amount of the polymer product under the same conditions.
(Table S1, run 4). The lack of activity of 2 for the homopolymerization of \textbf{AP} is probably due to the steric hindrance of the bulky C$_5$Me$_4$SiMe$_3$ ligand, which may hamper the continuous coordination/insertion of the sterically demanding \textbf{AP} monomer.

\textbf{3. Characterization of homopolymers of \textbf{AP}.}

\begin{center}
\includegraphics[width=0.5\textwidth]{syndiotactic_homopolymer}
\end{center}

100\% yield, $M_n = 13.2 \times 10^3$ g mol$^{-1}$, $M_w/M_n = 1.71$, $T_g = 68$ °C, $T_m = 152$ °C, \textit{rrrr} > 99\%.

$^1$H NMR (500 MHz, Chloroform-$d$) δ 7.09 (t, $J = 7.4$ Hz, 1H), 6.89 (d, $J = 6.9$ Hz, 1H), 6.77 (t, $J = 7.3$ Hz, 1H), 6.70 (d, $J = 8.2$ Hz, 1H), 3.52 (s, 3H), 2.31 (s, 2H), 1.72 (s, 1H), 0.72 (s, 2H). $^{13}$C\{$^1$H\} NMR (125 MHz, Chloroform-$d$) δ 157.7, 130.8, 130.7, 126.3, 119.9, 110.1, 54.9, 39.7, 35.4, 32.3.

\begin{center}
\includegraphics[width=0.5\textwidth]{NMR_spectrum}
\end{center}

$^1$H NMR (CDCl$_3$, 500 MHz, 26.8 °C)

\textbf{Figure S1.} $^1$H NMR Spectrum of syndiotactic homopolymer of \textbf{AP} (Table S1, run 3).
Figure S2. $^{13}$C{$^1$H} NMR Spectrum of syndiotactic homopolymer of AP (Table S1, run 3).

Figure S3. DEPT$^{135}$C NMR Spectrum of syndiotactic homopolymer of AP (Table S1, run 3).
**Figure S4.** HSQC spectrum of syndiotactic homopolymer of AP (Table S1, run 3)

**Figure S5.** HMBC spectrum of syndiotactic homopolymer of AP (Table S1, run 3)
Figure S6. H,H-COSY spectrum of syndiotactic homopolymer of AP (Table S1, run 3)

Figure S7. GPC curve of syndiotactic homopolymer of AP (Table S1, run 1)
Figure S8. GPC curve of syndiotactic homopolymer of AP (Table S1, run 2)

Figure S9. GPC curve of syndiotactic homopolymer of AP (Table S1, run 3)
Figure S10. DSC curve of syndiotactic homopolymer of AP (Table S1, run 1).

Figure S11. DSC curve of syndiotactic homopolymer of AP (Table S1, run 3).
4. Preparation of substituted 3-(2-anisyl)-1-propylene (\(A^R_P\)).

According to literature procedures \(^{53,54}\), the substituted 2-bromoanisole was converted to substituted 3-(2-anisyl)-1-propylene (\(A^R_P\)) by conversion to the Grignard reagent and coupling with allyl bromide.

**Typical procedure for the preparation of \(A^R_P\) (taking \(A^{Me}_P\) as an example).**

In nitrogen atmosphere, magnesium turnings (3.3 g, 0.14 mol), anhydrous lithium chloride (5.3 g, 0.12 mol), a catalytic amount of iodine (0.05 g, 0.2 mmol) and 300 mL anhydrous tetrahydrofuran were added to a 500 mL 3-neck flask. The reaction mixture was heated to reflux and 2-bromo-4-methylanisole (25.0 g, 0.12 mol) was added dropwise. After stirring for another 1 hour at room temperature, allyl bromide (22.6 g, 0.19 mol) was added slowly. The reaction mixture was then stirred overnight and quenched with saturated ammonium chloride aqueous solution. The crude product was purified through silica gel column chromatography (n-hexane) to give colourless liquid (17.0 g, 84%).
5. Characterization of substituted 3-(2-anisyl)-1-propylene (APR).

Figure S12. $^1$H NMR spectrum (500 MHz, #CDCl$_3$, * moisture in CDCl$_3$) of APR.

Figure S13. $^{13}$C{$^1$H} NMR spectrum (125 MHz, #CDCl$_3$) of APR.
Figure S14. $^1$H NMR spectrum (500 MHz, CDCl$_3$) of A$^{HexP}$.

Figure S15. $^{13}$C{$^1$H} NMR spectrum (125 MHz, CDCl$_3$) of A$^{HexP}$. 
Figure S16. $^1$H NMR spectrum (500 MHz, # CDCl$_3$, * moisture in CDCl$_3$) of A$^{Bu}$P.

Figure S17. $^{13}$C{$^1$H} NMR spectrum (125 MHz, # CDCl$_3$) of A$^{Bu}$P.
Figure S18. $^1$H NMR spectrum (500 MHz, $^6$CD$_6$) of AF$_P$.

Figure S19. $^{13}$C\{$^1$H\} NMR spectrum (125 MHz, $^6$CD$_6$) of AF$_P$. 
Figure S20. $^1\text{H}$ NMR spectrum (500 MHz, # CDCl$_3$, * moisture in CDCl$_3$) of A$^{\text{ClP}}$.

Figure S21. $^{13}\text{C}^{'\text{H}}$ NMR spectrum (125 MHz, # CDCl$_3$) of A$^{\text{ClP}}$. 
Figure S22. $^1$H NMR spectrum (500 MHz, CDCl$_3$, * moisture in CDCl$_3$) of A$^{\text{Naph}}$P.

Figure S23. $^{13}$C{$_1$H} NMR spectrum (125 MHz, CDCl$_3$) of A$^{\text{Naph}}$P.
6. General procedure for the copolymerization of AP with ethylene (Table 1, run 3)

In a THF-free glovebox, a toluene solution (150 mL) of AP (740 mg, 5 mmol) was charged into a three-necked flask with a magnetic stir bar. The flask was taken outside, set in a water bath (20 °C), and connected to a well-purged Schlenk ethylene line and a paraffin oil-sealed stopper by use of a three-way cock. Ethylene (1 atm) was introduced into the system and was saturated in the solution by stirring for 2 min. A toluene solution (2 mL) of \((\text{C}_5\text{Me}_4\text{SiMe}_3)\text{Sc(\C_6\text{H}_5\text{NMe}_2-6\text{-o})}_2\) (2) (5.1 mg, 0.01 mmol) and [Ph₃C][B(C₆F₅)₄] (9.2 mg, 0.01 mmol) was then added through a syringe under vigorous stirring. The polymerization was quenched after 5 minutes by adding methanol (150 mL). The polymer product was collected by filtration, washed with methanol, and then dried in vacuum at 60 °C to a constant weight (0.91 g). The resulting polymer was soluble in hot toluene, dichlorobenzene and 1,1,2,2-tetrachloroethane. Solvent fractionation experiments suggest that no homopolyethylene was formed. The AP content in the copolymer was calculated from the \(^1\text{H}\) NMR analysis.
Table S2. Scandium-catalyzed copolymerization of ethylene (E) and substituted 3-(2-anisyI)-1-propylene (AP)\textsuperscript{a}

\[
\begin{align*}
\text{R} & \quad \text{AP} \quad \text{E} \\
\text{AP-alt-E} & \quad \text{AP}_{\text{Me}}\text{-alt-E} \quad \text{AP}_{\text{Hex}}\text{-alt-E} \quad \text{AP}_{\text{Bu}}\text{-alt-E} \quad \text{AP}_{\text{F}}\text{-alt-E} \quad \text{AP}_{\text{Cl}}\text{-alt-E} \quad \text{AP}_{\text{Naph}}\text{-alt-E}
\end{align*}
\]

| Run | [AP\textsuperscript{R}] | [AP\textsuperscript{B}]/[Sc] \textsuperscript{b} | Time (h) | Yield (g) \textsuperscript{c} | Activity (g mol\textsuperscript{-1} atm\textsuperscript{-1}) | \(M_n\) \textsuperscript{d} (×10\textsuperscript{3}) | \(M_w/M_n\) \textsuperscript{d} | AP\textsuperscript{B}/E \textsuperscript{e} | \(T_g\) \textsuperscript{f} (°C) |
|-----|-----------------|-----------------|--------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1   | 200/1           |                 | 15 min | 0.70            | 1.4 × 10\textsuperscript{5} | 41 (P1)         | 1.7             | 39/61           | -6              |
| 2   | 500/1           |                 | 5 min  | 0.91            | 1.1 × 10\textsuperscript{6} | 90 (P2)         | 1.6             | 39/61           | -4              |
| 3   | 1000/1          |                 | 15 min | 1.61            | 6.4 × 10\textsuperscript{5} | 173 (P3)        | 1.9             | 41/59           | 4               |
| 4   | 2000/1          |                 | 6 h    | 3.05            | 5.1 × 10\textsuperscript{4} | 344 (P4)        | 1.7             | 45/55           | 5               |
| 5   | 5000/1          |                 | 24 h   | 8.35            | 3.5 × 10\textsuperscript{4} | 552 (P5)        | 2.0             | 46/54           | 6               |
| 6   | 500/1 \textsuperscript{g} |     | 1.5    | 1.96            | 6.5 × 10\textsuperscript{4} | 105 (P6')       | 1.8             | 42/58           | 9               |
| 7   | 2000/1          |                 | 9      | 3.35            | 3.7 × 10\textsuperscript{4} | 420 (P6)        | 1.6             | 38/62           | 11              |
| 8   | 500/1 \textsuperscript{g} |     | 2.5    | 2.43            | 4.9 × 10\textsuperscript{4} | 164 (P7')       | 1.5             | 36/64           | -31             |
| 9   | 2000/1          |                 | 20     | 4.33            | 2.2 × 10\textsuperscript{4} | 464 (P7)        | 1.7             | 42/58           | -28             |
| 10  | 500/1 \textsuperscript{g} |     | 4.5    | 1.96            | 2.2 × 10\textsuperscript{4} | 150 (P8')       | 1.8             | 42/58           | 23              |
| 11  | 2000/1          |                 | 48     | 4.11            | 8.0 × 10\textsuperscript{4} | 424 (P8)        | 1.7             | 42/58           | 21              |
| 12  | 500/1 \textsuperscript{g} |     | 10 min | 1.88            | 5.6 × 10\textsuperscript{5} | 124 (P9')       | 1.9             | 42/58           | 5               |
| 13  | 5000/1          |                 | 10     | 7.94            | 7.9 × 10\textsuperscript{4} | 446 (P9)        | 1.8             | 46/54           | 4               |
| 14  | 500/1 \textsuperscript{g} |     | 15 min | 2.20            | 4.4 × 10\textsuperscript{5} | 202 (P10')      | 2.1             | 38/42           | 18              |
| 15  | 2000/1          |                 | 1.1    | 3.89            | 3.5 × 10\textsuperscript{5} | 424 (10)        | 2.0             | 39/61           | 18              |
| 16  | 500/1 \textsuperscript{g} |     | 2      | 2.00            | 5.0 × 10\textsuperscript{4} | 115 (P11')      | 2.0             | 41/59           | 52              |
| 17  | 2000/1          |                 | 16     | 3.85            | 2.4 × 10\textsuperscript{4} | 259 (P11)       | 1.8             | 41/59           | 47              |

\textsuperscript{a} Conditions: [Sc] (0.01 mmol), [Ph\textsubscript{3}C][B(C\textsubscript{6}F\textsubscript{5})\textsubscript{4}] (B) (0.01 mmol), ethylene (1 atm), 150 mL toluene, 20 °C, unless otherwise noted. \textsuperscript{b} Feed ratio (in mole) of substituted o-anisyl propylene (AP\textsuperscript{B}) and a scandium complex. \textsuperscript{c} Gram of the polymer product. \textsuperscript{d} Determined by gel permeation chromatography (GPC) in o-dichlorobenzene at 140 °C against polystyrene standard. \(M_n\) = number average molecular weight, \(M_w\) = weight average molecular weight. \textsuperscript{e} Molar ratio of o-anisyl propylene (AP\textsuperscript{B}) and ethylene (E) in the copolymer, determined by \textsuperscript{1}H nuclear magnetic resonance (NMR) analysis. \textsuperscript{f} Determined by differential scanning calorimetry (DSC). \textsuperscript{g} [Sc] = [B] = 0.02 mmol, 50 mL toluene.

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Table S3. Scandium-catalyzed copolymerization of ethylene (E) and substituted 3-(2-anisyl)-1-propylene in different ethylene pressure.$^a$

![Chemical structure of the reaction](image)

| Run | Sc[mmol] | AP (g) | E | Yield (g) $^c$ | Conv. (AP) | Time (min) | $M_n$ ($10^3$ g mol$^{-1}$) $^d$ | $M_w/M_n$ | AP/E $^e$ | $T_m/T_g$ (°C) $^f$ |
|-----|---------|-------|---|--------------|-----------|-----------|-------------------------|---------|--------|----------------|
| 1   | 0.01    | 0.74  | 1 atm | 0.91         | 95%       | 5 min     | 90 (P2)                 | 1.6     | 39/61  | -6/124          |
| 2   | 0.06    | 2.96  | 2.1g (15 atm) | 4.31       | 94%       | 7 min     | 150 (P2')               | 1.7     | 24/76  | -15/118         |
| 3   | 0.06    | 1.48  | 2.6g (18 atm) | 2.70       | 91%       | 10 min    | 10 (P2'')               | 1.7     | 16/84  | -23/119         |

$^a$ Conditions: [Sc] = [Ph$_3$C][B(C$_6$F$_5$)$_4$], 50 mL toluene, 20 °C. $^b$ Ethylene pressure. $^c$ Gram of the polymer product. $^d$ Determined by gel permeation chromatography (GPC) in o-dichlorobenzene at 140 °C against polystyrene standard. $M_n$ = number average molecular weight, $M_w$ = weight average molecular weight. $^e$ Molar ratio of o-anisyl propylene (AP) and ethylene (E) in the copolymer, determined by $^1$H nuclear magnetic resonance (NMR) analysis. $^f$ Determined by differential scanning calorimetry (DSC).
7. Characterization of copolymers

Figure S24. $^1$H NMR spectrum (500 MHz, CDCl$_3$, 26.8 °C) of P1 (Table 1, run 2).

Figure S25. $^{13}$C($^1$H) NMR spectra (125 MHz, CDCl$_3$, 26.8 °C) of P1 (Table 1, run 2)
Figure S26. Partial enlargement of $^{13}\text{C} \{^1\text{H}\}$ NMR spectra (125 MHz, CDCl$_3$, 26.8 °C) of P1 (Table 1, run 2)

AP-$\alpha$-AP % = $\frac{C_{12}/(C_{12}+C_{14}/2+C_{16}/2+C_{18}/2)}{100\%} = 67\%$

AP-$t$-$t$-AP % = $\frac{(C_{14}/2+C_{16}/2)/(C_{12}+C_{14}/2+C_{16}/2+C_{18}/2)}{100\%} = 33\%$

AP-$AP$ % = $\frac{(C_{16}/2)/(C_{12}+C_{14}/2+C_{16}/2+C_{18}/2)}{100\%} = 0\%$

Figure S27. DSC curve of P1 (Table 1, run 2)
**Figure S28.** GPC curve of P1 (Table 1, run 2)

| Peak 1 Base Peak | [min] | [mV] | [mol] | Mn   | Mw   | Mz   | Mz+1 | Mz+1/Mw |
|------------------|-------|------|-------|------|------|------|------|---------|
| Peak start       | 7.378 | 0.123| 296.271| 41,060 | 68,764 | 95,680 | 119,011 | 68,764   |
| Peak top         | 8.132 | 51.091| 72.315 |      |      |      |      |         |
| Peak end         | 9.722 | 0.582| 3.278 |      |      |      |      |         |
| Height [mV]      | 50.620|      |       |      |      |      |      |         |
| Area [mV/s]      | 2559.562|   |       |      |      |      |      |         |
| Area% [%]        | 100.000|   |       |      |      |      |      |         |
| [n]              | 68763.89439|   |       |      |      |      |      |         |

Figure S29. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P2 (Table 1, run 3).
Figure S30. $^{13}$C$\{^{1}H\}$ NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P2 (Table 1, run 3).

Figure S31. Partial enlargement of $^{13}$C$\{^{1}H\}$ NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P2 (Table 1, run 3)
Figure S32. DSC curve of P2 (Table 1, run 3)

Figure S33. GPC curve of P2 (Table 1, run 3).
$n_{AP} = 1$

$n_{Ethylene} = H^{568}/4 = (14.58-2)/4 = 3.15$

$AP\ mol\% = n_{AP}/(n_{AP} + n_{Ethylene}) = 1/(1 + 3.15) = 24\ mol\%$

**Figure S34.** $^1H$ NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P2' (Table S3, run 2).

**Figure S35.** $^{13}C\{^{1H}\} NMR$ spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P2' (Table S3, run 2).
Figure S36. DSC curve of P2' (Table S3, run 2).

Figure S37. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P2'' (Table S3, run 3).
Figure S38. $^{13}$C($^{1}$H) NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P2'' (Table S3, run 3).

Figure S39. DSC curve of P2'' (Table S3, run 3).
Figure S40. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P3 (Table 1, run 4).

Figure S41. $^{13}$C{$^1$H} NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P3 (Table 1, run 4).
Figure S42. Partial enlargement of $^{13}$C-$^1$H NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P3 (Table 1, run 4).

Figure S43. DSC curve of P3 (Table 1, run 4).
Figure S44. GPC curve of P3 (Table 1, run 4).

\[
\begin{align*}
n^{\text{AP}} &= 1 \\
n^{\text{Ethylene}} &= \frac{\text{H}^{564}}{4} = \frac{6.93 - 2}{4} = 1.23 \\
\text{AP mol\%} &= \frac{n^{\text{AP}}}{(n^{\text{AP}} + n^{\text{Ethylene}})} = \frac{1}{1 + 1.23} = 45 \text{ mol\%}
\end{align*}
\]

Figure S45. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P4 (Table 1, run 5).
Figure S46. $^{13}$C$\left\{^1\text{H}\right\}$ NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P4 (Table 1, run 5).

Figure S47. Partial enlargement of $^{13}$C$\left\{^1\text{H}\right\}$ NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P4 (Table 1, run 5)
**Figure S48.** DSC curve of P4 (Table 1, run 5).

**Figure S49.** GPC curve of P4 (Table 1, run 5).
$n^{AP} = 1$

$n^{Ethylene} = H^{5,6,7,8/4} = (6.7\cdot2)/4 = 1.17$

$AP \text{ mol}\% = n^{AP}/(n^{AP}+n^{Ethylene}) = 1/(1 + 1.17) = 46 \text{ mol}\%$

**Figure S50.** $^1H$ NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P5 (Table 1, run 6).

**Figure S51.** $^{13}C\{^1H\}$ NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P5 (Table 1, run 6).
Figure S52. Partial enlargement of $^{13}$C{$^{1}$H} NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 26.8 °C) of P5 (Table 1, run 6).

Figure S53. DEPT$^{135}$C NMR Spectrum (C$_2$D$_2$Cl$_4$) of P5 (Table 1, run 6).
Figure S54. HSQC spectrum (C$_2$D$_2$Cl$_4$) of P5 (Table 1, run 6).

Figure S55. HMBC spectrum (C$_2$D$_2$Cl$_4$) of P5 (Table 1, run 6).
Figure S56. H-C COSY spectrum ($\text{C}_2\text{D}_2\text{Cl}_4$) of P5 (Table 1, run 6).

Figure S57. HETCOR spectrum ($\text{C}_2\text{D}_2\text{Cl}_4$) of P5 (Table 1, run 6).
Figure S58. DSC curve of P5 (Table 1, run 6).

Figure S59. GPC curve of P5 (Table 1, run 6).
Figure S60. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of E-AB copolymer

Figure S61. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P6 (Table S2, run 7).
Figure S62. $^{13}$C{$^1$H} NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P6 (Table S2, run 7).

Figure S63. Partial enlargement of $^{13}$C{$^1$H} NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P6 (Table S2, run 7).
**Figure S64.** DEPT$^{135}$C NMR Spectrum (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P6 (Table S2, run 7).

**Supplementary Figure 65.** DSC curve of P6 (Table S2, run 7).
**Figure S66.** GPC curve of P6 (Table S2, run 7).

**Figure S67.** GPC curve of P6’ (Table S2, run 6).
Figure S68. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P7 (Table S2, run 9).

Figure S69. $^{13}$C{$^1$H} NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P7 (Table S2, run 9).
Figure S70. DEPT\textsuperscript{135}C NMR Spectrum (125 MHz, $C_2D_2Cl_4$, 120 °C) of P7 (Table S2, run 9).

Figure S71. DSC curve of P7 (Table S2, run 9).
Figure S72. GPC curve of P7 (Table S2, run 9).

Figure S73. GPC curve of P7' (Table S2, run 8).
Figure S74. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P8 (Table S2, run 11).

Figure S75. $^{13}$C{$_1^1$H} NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P8 (Table S2, run 11).
Figure S76. DEPT$^{135}$C NMR Spectrum (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P8 (Table S2, run 11).

Figure S77. DSC curve of P8 (Table S2, run 11).
Figure S78. GPC curve of P8 (Table S2, run 11).

Figure S79. GPC curve of P8' (Table S2, run 10).
$^1$H NMR ($C_2D_2Cl_4$, 500 MHz, 26.8 °C)

$n^{AP} = 1$

$n^{Ethylene} = H^{5,6,7,8} / 4 = (6.72 - 2) / 4 = 1.18$

AP mol% = $n^{AP} / (n^{AP} + n^{Ethylene}) = 1 / (1 + 1.18) = 45.9$ mol%

Figure S80. $^1$H NMR spectrum (500 MHz, $C_2D_2Cl_4$, 120 °C) of $P9$ (Table S2, run 13).

$^{13}C\{^1H\}$ NMR spectra (125 MHz, $C_2D_2Cl_4$, 120 °C) of $P9$ (Table S2, run 13).
Figure S82. DEPT$^{135}$C NMR Spectrum (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P9 (Table S2, run 13).

Figure S83. DSC curve of P9 (Table S2, run 13).
Figure S84. GPC curve of P9 (Table S2, run 13).

Figure S85. GPC curve of P9' (Table S2, run 12).
Figure S86. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P10 (Table S2, run 15).

Figure S87. $^{13}$C{$^1$H} NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P10 (Table S2, run 15).
Figure S88. DEPT$^{13}$C NMR Spectrum (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P10 (Table S2, run 15).

Figure S89. DSC curve of P10 (Table S2, run 15).
Figure S90. GPC curve of P10' (Table S2, run 14).

Figure S91. GPC curve of P10 (Table S2, run 15).
Figure S92. $^1$H NMR spectrum (500 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P11 (Table S2, run 17).

Figure S93. $^{13}$C($^1$H) NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P11 (Table S2, run 17).
Figure S94. DEPT$^{135}$C NMR Spectrum (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P11 (Table S2, run 17).

Figure S95. DSC curve of P11 (Table S2, run 17).
Figure S96. GPC curve of P11 (Table S2, run 17).

Figure S97. GPC curve of P11' (Table S2, run 16).
Scheme S1. Synthesis of P2-OH.

**Synthesis of HO-containing polymer P2-OH.** According to the reported procedure, under a nitrogen atmosphere, boron tribromide (10 g, 40 mmol) was added slowly dropwise to a CH₂Cl₂ solution (200 mL) of P2 (3.3 g, 20 mmol based on polar monomer) at 0 °C in a 500 mL three-necked flask and was stirred for 1 h. The reaction solution was warmed to room temperature and then stirred for a further 24 h. The orange solution was subsequently cooled in an ice bath, and 100 mL of deionized water was added. Following evolution of fumes, the mixture was slowly warmed to room temperature. The precipitate was collected by filtration and sequentially washed with water and CH₂Cl₂, before the resultant white powder was dried. The product became brown-colored brittle material (3.1 g, 99%) when the material was heat (100 °C) in vacuum for 12 hours to remove solvent. The molecular weight has not been test because the product is insoluble in hot 1, 2-dichlorobenzene.

![NMR spectrum](image)

**Figure S98.** $^1$H NMR spectrum (500 MHz, C₂D₂Cl₄, 120 °C) of P2-OH.
Figure S99. $^{13}$C{$^{1}$H} NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P2-OH.

Figure S100. DSC curve of P2-OH.
Scheme S2. Synthesis of P2-OSiEt3.

Synthesis of Et₃SiO-substituted polymer P2-OSiEt₃. According to the reported procedure, in a nitrogen-filled glovebox, to a solution of P2 (3.3 g, 20 mmol based on polar monomer) in CH₂Cl₂ (100 mL) was added B(C₆F₅)₃ (538.0 mg, 5 mol% based on polar monomer) and Et₃SiH (7.32 g, 60 mmol). The resulting solution was stirred at room temperature for 12 hours, and then carefully quenched by adding MeOH. The viscous precipitation was collected and dried under vacuum at 60 °C to a constant weight (5.2 g.). The molecular weight has not been test because the product was partially decomposed in hot 1, 2-dichlorobenzene.

Figure S101. $^1$H NMR spectrum (500 MHz, C₂D₂Cl₄, 120 °C) of P2-OSiEt₃.
Figure S102. $^{13}\text{C}\{^1\text{H}\}$ NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P2-OSiEt$_3$.

Figure S103. DSC curve of P2-OSiEt$_3$. 
Scheme S3. Synthesis of P2-Cy.

Synthesis of P2-Cy. According to the reported procedure, under a nitrogen atmosphere, a mixture of P2 (3.0g, ~18.5 mmol), Rh/Al2O3 (3 g, 5 wt%) and 100 mL THF was hydrogenated at 80 MPa hydrogen pressure at 80 °C. The catalyst was removed by filtration, and the filtrate was concentrated in vacuo to 3.2 g of P2-Cy (100%) as a colorless solid.

Figure S104. 1H NMR spectrum (500 MHz, C2D2Cl4, 120 °C) of P2-Cy.
**Figure S105.** $^{13}$C($^1$H) NMR spectra (125 MHz, C$_2$D$_2$Cl$_4$, 120 °C) of P2-Cy.

**Figure S106.** DSC curve of P2-Cy.
8. Mechanical and self-healing tests

Dynamic mechanical measurements were performed on a RSA III straincontrolled rheometer (TA Instruments) with parallel plate configuration. A rectangular shape sample was clamped in a gauge length of 15 mm. The measurements were carried out at 11 Hz frequency under a dry nitrogen atmosphere at a heating rate of 2 °C min$^{-1}$ over the temperature range from −50 to 150 °C. The thermal mechanical analysis experiments were performed using a TMA/SS6100 instument (Hitachi High-Tech Science Co.) under a dry nitrogen atmosphere at a heating rate of 3 °C min$^{-1}$.

Mechanical tensile-stress experiments were performed using an Instron 3342 instrument. Three samples were tested for each polymer composition. Tensile experiments were performed at room temperature (25±1 °C) at different sample size and strain rate when evaluating the stretchability according to ASTM 882-09 test method using dumbbell configured specimens according to JIS K-6251-7 (width: 2 mm; length: 12 mm; thickness: 1 mm). High temperature tensile-stress experiments were performed using an AG-X plus Series (SHIMADZU) with a TCE-N300 with thermostatic chamber. Strain at break and stress at break experiment was determined at fracture using uniaxial tensile test with a strain rate of 200 mm/min. Young’s modulus is the initial slope of the nominal stress vs nominal strain curve in the linear region (0 < $\varepsilon$ < 0.05) and was calculated from the average of three monotonic curves. Cyclic stress-strain test for P1-P5 was carried out with a strain rate of 200 mm/min and release rate of 20 mm/min. Strain recovery was determined by a 1000% strain step cycle test using the equation $100(\varepsilon_a - \varepsilon_t)/\varepsilon_a$, where $\varepsilon_a =$ applied strain and $\varepsilon_t =$ strain at zero load after 10th cycle. For self-healing tests, the sample was cut into separate parts completely using razor blade. The break surface of films was contacted in air, water, HCl and NaOH aqueous solution for different durations. The cut faces were brought together and gently pressed for less than 15 seconds at 25 °C. The healed polymer films were then stretched following the same procedure to obtain the stress-strain curves. The mechanical healing efficiency was defined as the ratio between the fracture strain restored relative to the original fracture strain.

Shape memory test. All quantitative shape memory properties were evaluated in a tensile and force controlled mode in a typical thermal mechanical analysis. The heating
and cooling rates were both 3 °C per minute. $R_f$ and $R_r$ for the dual-shape memory effect were calculated using equations (1) and (2) given below:

$$R_f = 100\% \times \varepsilon / \varepsilon_{load} \quad (1)$$

$$R_r = 100\% \times (\varepsilon - \varepsilon_{rec}) / \varepsilon \quad (2)$$

where $\varepsilon_{load}$ represents the maximum strain under load, $\varepsilon$ is the fixed strain after cooling and load removal, and $\varepsilon_{rec}$ is the strain after recovery.

**Figure S107.** Transmittance spectrum of a P2 film with 0.5 mm thickness.

**Figure S108.** Temperature dependence of the dynamic tensile storage modulus ($E'$, blue) and the dynamic tensile loss modulus ($E''$, red) of a P5 film at 11 Hz frequency.
Figure S109. The thermogravimetric analysis of P5.

Figure S110. The thermogravimetric analysis of low density polyethylene (Aldrich).

The thermostability of copolymer was examined by thermogravimetric analysis (TGA) in terms of onset decomposition temperature $T_d$ and maximum decomposition temperature $T_{\text{max}}$. The $T_d$ and $T_{\text{max}}$ of P5 were 409 °C and 478 °C (Supplementary Fig. 109) which were slightly lower than the commercial available low density polyethylene (436 °C and 485 °C, see Supplementary Fig. 110).
Figure S111. 2D-WAXS measurement of P5.

Figure S112. Tensile strength/hysteresis curves of P1-P4.
Figure S113. Tensile strength/hysteresis curves of P5.

Figure S114. The stress–strain curves of P2 and P2-OSiEt₃ measured in a speed of 200 mm min⁻¹.
Figure S115. The stress–strain curves of P2 and P2-Cy measured in a speed of 200 mm min⁻¹.

Figure S116. Self-healing tests of P2 (i, ii), P2′ (iii, iv) and P2″ (v) in air at 25 °C.

Figure S117. Tensile strength/hysteresis curves of P2′ and P2″.
Figure S118. The stress–strain curves of $P_6'$ and $P_9'$ measured in a speed of 200 mm min$^{-1}$.

Figure S119. The stress–strain curves of $P_8'$ and $P_{10}'$ measured in a speed of 200 mm min$^{-1}$ (left) and 20 mm min$^{-1}$ (right).

Figure S120. The stress–strain curves of $P_7'$ measured in a speed of 200 mm min$^{-1}$ (sample size: 1 mm thickness, 2 mm width, 4 mm length).
Figure S121. Tensile strength/hysteresis curves of (A) P6, (B) P7, (C) P8, (D) P9 and (E) P10.
Figure S122. The stress strain curves of P7 at low temperatures.

Figure S123. The stress strain curves of P8 at various temperatures.

Figure S124. Self-healing tests of (A) P7', (B) P9' and (C) P6' in air at 25 °C.
**Figure S125.** Self-healing tests of P2 healed in air and N2-filled glovebox and at 25 °C.

**Figure S126. Shape memory property of P11.** (A), Original shapes. (B), The tailored samples were stretched in a 80 °C-water bath and fixed at room temperature when the force was removed. (C), The original shapes were recovered in the 80 °C-water bath in 2 minutes.
Table S4. Summary of mechanical and self-healing properties of E-AP\textsuperscript{R} copolymers.\textsuperscript{a}

|     | \(M_n\) (kDa) | Virgin | | Healing | Repaired |
|-----|----------------|--------|---------------------------------|------------|----------|
|     |                | Initial modulus (MPa) | Tensile strength (MPa) | Elongation at break (%) | Toughness (MJ/m\(^3\)) | Tensile strength (MPa) | Elongation at break (%) | Toughness (MJ/m\(^3\)) |
| P5  | 552            | 13.5±0.3        | 10.2±0.6                          | 2054±18\(^5\) | 68.2±11.0  | 120/90%            | 6.7                    | 1520                  | 34.6                  |
| P6  | 420            | 139.6±25.5      | 17.7±0.3                          | 1272±52      | 84.8±4.8   | 120/87%            | 12.6                   | 1117                  | 49.7                  |
| P7  | 464            | 4.3             | <0.1                              | >10000       | 1.71       | 1/100%             | <0.1                   | >10000                 | 1.71                  |
| P8  | 424            | 467.9±22.9      | 15.6±0.8                          | 565±5        | 66.1±2.2   | -                   | -                     | -                     | -                     |
| P9  | 450            | 28.5±2.8        | 16.6±0.6                          | 1454±47      | 72.4±6.5   | 120/86%            | 11.9                   | 1303                  | 47.2                  |
| P10 | 389            | 218±34          | 21.7±0.9                          | 954±51       | 117.0±8.6  | -                   | -                     | -                     | -                     |
| P11 | 259            | 1221.6±54.5     | 52.1±0.3                          | 7±1          | 1.9±0.3    | -                   | -                     | -                     | -                     |

\textsuperscript{a} For self-healing tests, the film sample (sample size: 1 mm thickness, 2 mm width, 12 mm length in the middle) was cut by a razor and then brought together at room temperature. \textsuperscript{b} Self-healing efficiency was calculated based on the recovery ratio of repaired elongation at break versus virgin elongation at break.

9. Movies.

**Movie 1.** This movie shows a fast self-healing phenomenon of a film of polymer P5 at room temperature.

**Movie 2.** This movie shows a fast self-healing phenomenon of a 5 mm thickness board of polymer P2 at room temperature. The rapid self-healed sample could load higher than 1.2 kg weight.

**Movie 3.** This movie shows a fast self-healing phenomenon of a film of polymer P7 in ice water (0 °C).

**Movie 4.** This movie shows a slow self-healing phenomenon of a film of polymer P8 at room temperature in air at room temperature, and fast healing in hot water (50 °C). When the hot water was poured over the cut polymer film, the scar disappeared within a few minutes.
10. References.

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