

# Supplementary material for Study of PVAc/EVA Polymer Series: Influence of the Inter/Intra - molecular Interaction Ratio on the Molecular Mobility at the Glass Transition

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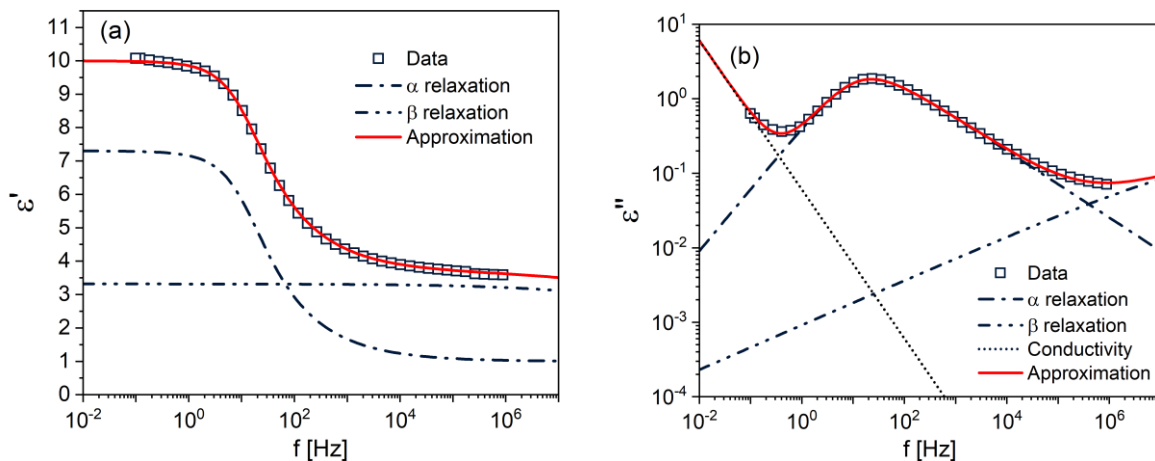
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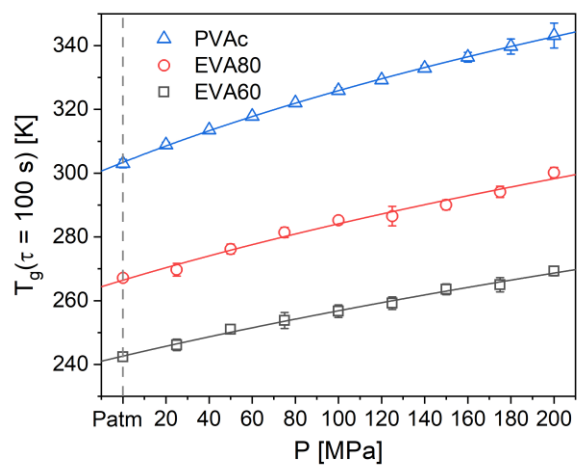
## SUPPLEMENTARY TEXT

*Example of dielectric spectrum approximation.* The dielectric relaxation curves obtained were analyzed using the Havriliak-Negami (HN) complex function. An example of a dielectric spectrum approximation using the HN fitting function and conductivity is shown in **Fig. S1**.

*Pressure dependency of the glass transition temperature.* The pressure influence on  $T_g$  for the PVAc/EVA series is shown in **Fig. S2**. The nonlinear relationship between  $T_g$  and pressure can be fitted by the empirical Andersson-Andersson model.



**FIG. S1.** Example of approximation to (a) the real and (b) the imaginary part of the complex permittivity at  $P = 15$  MPa and  $T = 329$  K for PVAc. Experimental data are represented by empty squares. The red curves correspond to the sum the contributions from conductivity (dotted line),  $\alpha$ -relaxation (dashed dotted lines) and  $\beta$ -relaxation (dashed double dotted lines).



**FIG. S2.** Pressure dependence of the glass transition temperature (from the extrapolation of VFT fit to  $\tau = 10$  s) for EVA60, EVA80 and PVAc. Solid red line indicates an experimental data fit to the Andersson–Andersson model.

**Table S1.** Parameters of HN fits for secondary relaxation and conductivity. For the secondary relaxation, the dielectric strength  $\Delta\varepsilon_\beta$  and the broadening parameters  $\alpha_{HN\beta}$  and  $\beta_{HN\beta}$  are constants. Only the ohmic conductivity  $\sigma_0$  and the secondary relaxation time  $\tau_\beta$  are considered temperature dependent.

|       | $\Delta\varepsilon_\beta$ | $\alpha_{HN\beta}$ | $\beta_{HN\beta}$ |
|-------|---------------------------|--------------------|-------------------|
| PVAc  | 1.32                      | 0.3                | 1                 |
| EVA80 | 1.00                      | 0.5                | 1                 |
| EVA60 | 0.65                      | 0.5                | 1                 |

Example of conductivity  $\sigma_0$  and the secondary relaxation time  $\tau_\beta$  as function of temperature at 100 MPa for PVAc, EVA80 and EVA60.

| PVAc |                             |                               | EVA80 |                             |                               | EVA60 |                             |                               |
|------|-----------------------------|-------------------------------|-------|-----------------------------|-------------------------------|-------|-----------------------------|-------------------------------|
| T    | $\text{Log}_{10}(\sigma_0)$ | $\text{Log}_{10}(\tau_\beta)$ | T     | $\text{Log}_{10}(\sigma_0)$ | $\text{Log}_{10}(\tau_\beta)$ | T     | $\text{Log}_{10}(\sigma_0)$ | $\text{Log}_{10}(\tau_\beta)$ |
| [K]  | [S. cm <sup>-1</sup> ]      | [s]                           | [K]   | [S. cm <sup>-1</sup> ]      | [s]                           | [K]   | [S. cm <sup>-1</sup> ]      | [s]                           |
| 331  | -13.7                       | -10.1                         | 301   | -14.4                       | -6.8                          | 268   | -14.6                       | -6.6                          |
| 333  | -13.7                       | -10.0                         | 303   | -14.3                       | -6.9                          | 270   | -18.4                       | -6.8                          |
| 335  | -13.7                       | -9.9                          | 305   | -14.2                       | -7.0                          | 272   | -14.9                       | -6.9                          |
| 337  | -13.8                       | -9.9                          | 307   | -14.1                       | -7.1                          | 273   | -14.7                       | -7.3                          |
| 339  | -13.8                       | -9.7                          | 309   | -14.1                       | -7.4                          | 275   | -14.8                       | -8.1                          |
| 341  | -13.8                       | -9.9                          | 311   | -14.0                       | -7.5                          | 277   | -14.8                       | -8.3                          |
| 343  | -13.7                       | -9.6                          | 313   | -14.0                       | -7.8                          | 279   | -14.9                       | -8.6                          |
| 345  | -13.6                       | -9.5                          | 315   | -13.9                       | -8.2                          | 281   | -15.1                       | -8.9                          |
| 347  | -13.6                       | -9.8                          | 317   | -13.7                       | -8.9                          | 283   | -15.0                       | -10.5                         |
| 349  | -13.5                       | -9.6                          | 319   | -13.6                       | -8.9                          | 285   | -15.0                       | -10.0                         |
|      |                             |                               | 322   | -13.5                       | -8.9                          | 287   | -14.9                       | -9.7                          |
|      |                             |                               | 324   | -13.4                       | -8.9                          | 289   | -14.8                       | -9.6                          |
|      |                             |                               | 326   | -13.3                       | -8.9                          | 291   | -14.8                       | -9.9                          |
|      |                             |                               | 328   | -13.1                       | -8.9                          | 293   | -14.7                       | -11.0                         |
|      |                             |                               | 330   | -13.0                       | -8.9                          | 295   | -14.5                       | -10.4                         |

**Table S2.** Frequency list of dielectric measurements shown in **Fig. 4**. The frequency range is from  $10^{-1}$  up to  $10^6$  Hz, and is composed of 42 measurements spaced logarithmically.

| f [Hz]   |          |          |          |          |          |          |
|----------|----------|----------|----------|----------|----------|----------|
| 1.00E+06 | 1.17E+05 | 1.03E+04 | 9.02E+02 | 7.92E+01 | 6.95E+00 | 6.11E-01 |
| 8.89E+05 | 7.80E+04 | 6.85E+03 | 6.02E+02 | 5.28E+01 | 4.64E+00 | 4.07E-01 |
| 5.93E+05 | 5.20E+04 | 4.57E+03 | 4.01E+02 | 3.52E+01 | 3.09E+00 | 2.71E-01 |
| 3.95E+05 | 3.47E+04 | 3.05E+03 | 2.67E+02 | 2.35E+01 | 2.06E+00 | 1.81E-01 |
| 2.63E+05 | 2.31E+04 | 2.03E+03 | 1.78E+02 | 1.56E+01 | 1.37E+00 | 1.21E-01 |
| 1.76E+05 | 1.54E+04 | 1.35E+03 | 1.19E+02 | 1.04E+01 | 9.16E-01 | 1.00E-01 |

**Table S3.** Fit parameters ( $\log(\tau_\infty)$ ,  $D$ ,  $T_0$ ), uncertainties of  $D$  and  $T_0$ , glass transition temperature  $T_g$ , isobaric fragility  $m_p$  and the R-squared of the VFT laws of isobars (**Eq. (2)** in the main manuscript) for PVAc, EVA80 and EVA60.

| EVA 60           |                         |       |            |           |                  |       |       |        |
|------------------|-------------------------|-------|------------|-----------|------------------|-------|-------|--------|
| $P$ [MPa]        | $\log(\tau_\infty)$ [s] | $D$   | $\Delta D$ | $T_0$ [K] | $\Delta T_0$ [K] | $T_g$ | $m_p$ | $R^2$  |
| $P_{\text{atm}}$ | -14                     | 8.94  | 0.08       | 195.07    | 0.46             | 246   | 73    | 0.9965 |
| 25               | -14                     | 9.33  | 0.15       | 195.30    | 0.87             | 248   | 71    | 0.9981 |
| 50               | -14                     | 8.84  | 0.12       | 202.46    | 0.71             | 254   | 74    | 0.9979 |
| 75               | -14                     | 9.17  | 0.24       | 203.19    | 1.37             | 257   | 71    | 0.9931 |
| 100              | -14                     | 9.09  | 0.21       | 205.88    | 1.19             | 260   | 72    | 0.9935 |
| 125              | -14                     | 9.21  | 0.22       | 207.39    | 1.24             | 263   | 71    | 0.9957 |
| 150              | -14                     | 9.13  | 0.19       | 211.20    | 1.07             | 267   | 72    | 0.9961 |
| 175              | -14                     | 9.62  | 0.24       | 210.13    | 1.38             | 269   | 69    | 0.9959 |
| 200              | -14                     | 10.10 | 0.16       | 211.32    | 0.93             | 273   | 66    | 0.9972 |

| EVA 80           |                         |       |            |           |                  |       |       |        |
|------------------|-------------------------|-------|------------|-----------|------------------|-------|-------|--------|
| $P$ [MPa]        | $\log(\tau_\infty)$ [s] | $D$   | $\Delta D$ | $T_0$ [K] | $\Delta T_0$ [K] | $T_g$ | $m_p$ | $R^2$  |
| $P_{\text{atm}}$ | -14                     | 10.04 | 0.13       | 209.94    | 0.77             | 271   | 82    | 0.9977 |
| 25               | -14                     | 10.39 | 0.22       | 210.40    | 1.31             | 274   | 79    | 0.9964 |
| 50               | -14                     | 10.50 | 0.23       | 214.94    | 1.38             | 280   | 83    | 0.9959 |
| 75               | -14                     | 10.08 | 0.16       | 220.97    | 0.99             | 285   | 80    | 0.9978 |

|     |     |       |      |        |      |     |    |        |
|-----|-----|-------|------|--------|------|-----|----|--------|
| 100 | -14 | 10.21 | 0.16 | 223.29 | 0.95 | 289 | 81 | 0.9981 |
| 125 | -14 | 10.58 | 0.27 | 222.58 | 1.63 | 291 | 80 | 0.9960 |
| 150 | -14 | 10.73 | 0.18 | 224.66 | 1.09 | 294 | 81 | 0.9977 |
| 175 | -14 | 10.68 | 0.21 | 228.02 | 1.28 | 299 | 77 | 0.9973 |
| 200 | -14 | 11.13 | 0.19 | 230.51 | 1.18 | 305 | 74 | 0.9973 |

PVAc

| $P$ [MPa]        | $\log(\tau_\infty[s])$ | $D$   | $\Delta D$ | $T_0$ [K] | $\Delta T_0$ [K] | $T_g$ | $m_p$ | $R^2$  |
|------------------|------------------------|-------|------------|-----------|------------------|-------|-------|--------|
| $P_{\text{atm}}$ | -14                    | 9.80  | 0.12       | 239.36    | 0.83             | 307   | 76    | 0.9984 |
| 20               | -14                    | 9.77  | 0.08       | 244.11    | 0.50             | 313   | 76    | 0.9993 |
| 40               | -14                    | 9.76  | 0.05       | 247.86    | 0.30             | 318   | 76    | 0.9998 |
| 60               | -14                    | 9.84  | 0.04       | 250.83    | 0.30             | 322   | 76    | 0.9998 |
| 80               | -14                    | 9.89  | 0.05       | 253.84    | 0.32             | 327   | 76    | 0.9997 |
| 100              | -14                    | 10.03 | 0.09       | 256.16    | 0.53             | 331   | 75    | 0.9993 |
| 120              | -14                    | 9.77  | 0.06       | 260.22    | 0.36             | 334   | 76    | 0.9997 |
| 140              | -14                    | 9.85  | 0.09       | 262.65    | 0.54             | 338   | 76    | 0.9994 |
| 160              | -14                    | 10.06 | 0.15       | 264.22    | 0.87             | 341   | 75    | 0.9984 |
| 180              | -14                    | 10.47 | 0.23       | 264.56    | 1.31             | 345   | 72    | 0.9969 |
| 200              | -14                    | 11.02 | 0.39       | 264.14    | 2.12             | 348   | 70    | 0.9930 |