Electronic Supplementary Material (ESI) for Journal of Materials Chemistry C.

Supplementary Information

Molecularly-Doped Polymer Foams with Massive Piezoelectric Response

*Michael J. Moody, Christopher W. Marvin, and Geoffrey R. Hutchison.**

Measurement Details

For measurement of quasistatic piezocoefficient, the sample electrodes were connected to one channel of a Keithly 2612 sourcemeter in ammeter configuration. A Tekscan Flexiforce A2013 resistive force was connected to another channel. A 1 V bias was applied to the Flexiforce sensor and the current was measured to calculate resistance. The force sensor has a reciprocal relation between applied force and resistance and had been previously calibrated with loads from 1 N to 60 N. The force sensor, electromagnetically shielded from the sample with copper tape, was placed over the sample in a stack consisting of a glass slide, the sample, another glass slide, the force sensor, and a PDMS spacer, and this was placed into a fixture consisting of a plastic contact point on a leadscrew operated manually.

Current and force data were collected every 34 ms over 70 s while varying forces were applied. Net charge transfer was calculated by numerically integrating the current signal (rectangle method). Example current, charge (with linear baseline correction), and force data are shown in **Figure S1**.

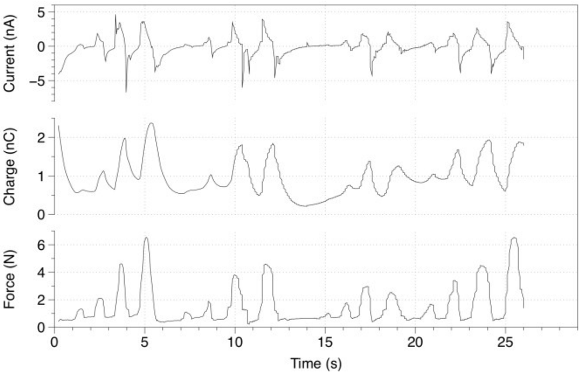

Figure S1: Measured current, charge (integrated current), and measured force over time during sample testing.

Figure 2a plots peak heights from the charge signal against peak heights from the force signal in **Figure S1**. Error bars are from the specified force sensor accuracy (5%) and Sourcemeter current accuracy multiplied by 1 second (18 pC). The charge is proportional to the force until a saturation point, apparently corresponding to compression of the foam to ~20 – 30% of its original thickness. Regression over the linear region gives the d_{33} piezocoefficient in pC N^{-1} with error bars from the fit. In cases where several measurements were made of the same condition (**Figure 2b**), error bars were the standard error across multiple samples.

This measurement setup was validated using commercial PVDF samples, which were measured to have piezocoefficients of 27.3 ± 4.0 pC/N, consistent with the reported value.

Use of Acetone as Dopant Solvent

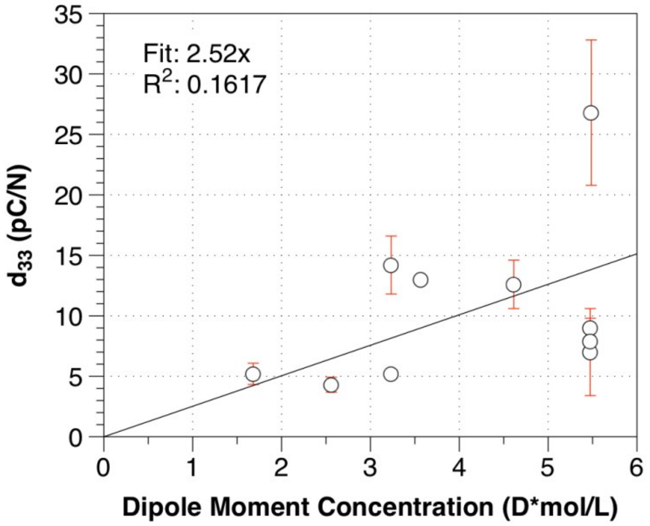

Figure S2: Piezocoefficient as a function of dipole moment concentration for samples prepared with added acetone.

Higher dopant concentrations were obtained with the addition of acetone. Although these data in **Figure S2**, also show a positive correlation between piezocoefficient and dipole moment concentration, it is a much weaker correlation ($R^2 = 0.161$) and with a lower slope than without acetone plotted in **Figure 1b**.

Effect of Humidity

It was also observed that increased ambient humidity had a negative influence on the piezocoefficient. Less than 10% of doped samples poled in lab conditions of relative humidity of 35 – 40% had responses distinguishable from control, in comparison to over 90% poled in relatively humidity of 20 – 25%. During periods of ambient humidity over 40%, precursors were mixed and poled in a glove bag with nitrogen fill (RH < 22%) and measured and stored in ambient conditions, leading to a yield of over 70%. Although the specific source of this influence is unknown, it may also be related to the reduction of response with added acetone. Glovebag samples showed somewhat higher responses than samples prepared in dry ambient conditions but follow the same trends.

Stability

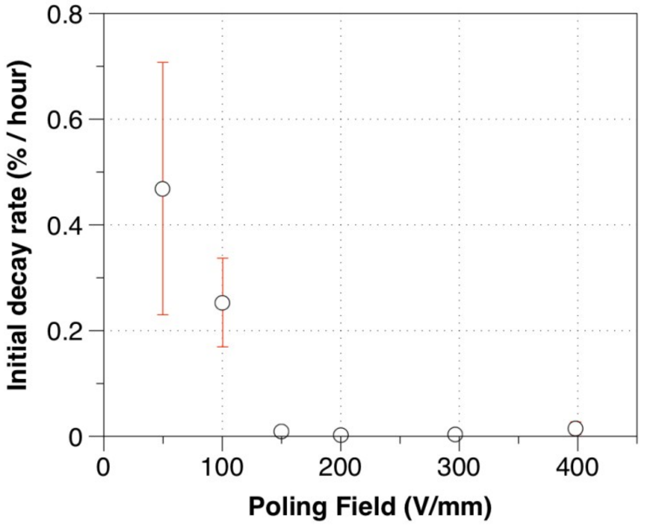

Figure S3: Initial decay rate of piezoresponse as a function of poling field.

CNA Structure

CNA crystallizes in a centrosymmetric structure, as shown below:

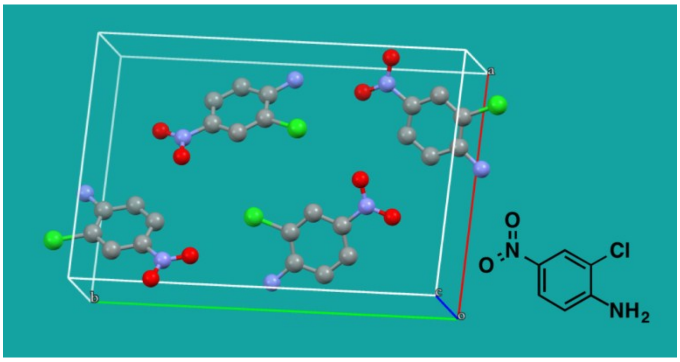

Figure S4: The crystal structure of 2-chloro-4-nitroaniline. (Structure data from [S1] via [S2])

Note that the unit cell is centrosymmetric

ϵ_∞ calculation

As ϵ_∞ represents the dielectric response in the absence of permanent dipole motion, it cannot be experimentally measured under quasistatic conditions. It can however, be estimated from the Clausius-Mossotti equation given in **Equation S1**.

$$\frac{\epsilon_\infty - 1}{\epsilon_\infty + 2}\epsilon_0 V_m = \frac{4\pi}{3}N\alpha \tag{S1}$$

where V_m is the molar volume, N is Avogadro's number, and α is the molecular polarizability.

For the case of benzoic acid ($\alpha \approx 2 \times 10^{-39}$ C^2 m^2 J^{-1}) [S3] at a concentration of 1 M, ϵ_∞ works out to be 5.0. A dielectric constant of 4 corresponds to a doubling of polarization with the factor of

$$\frac{\epsilon_\infty + 2}{3} \tag{S2}$$

and appears to be within the range of realistic materials.

Foam Void Dimension Measurements

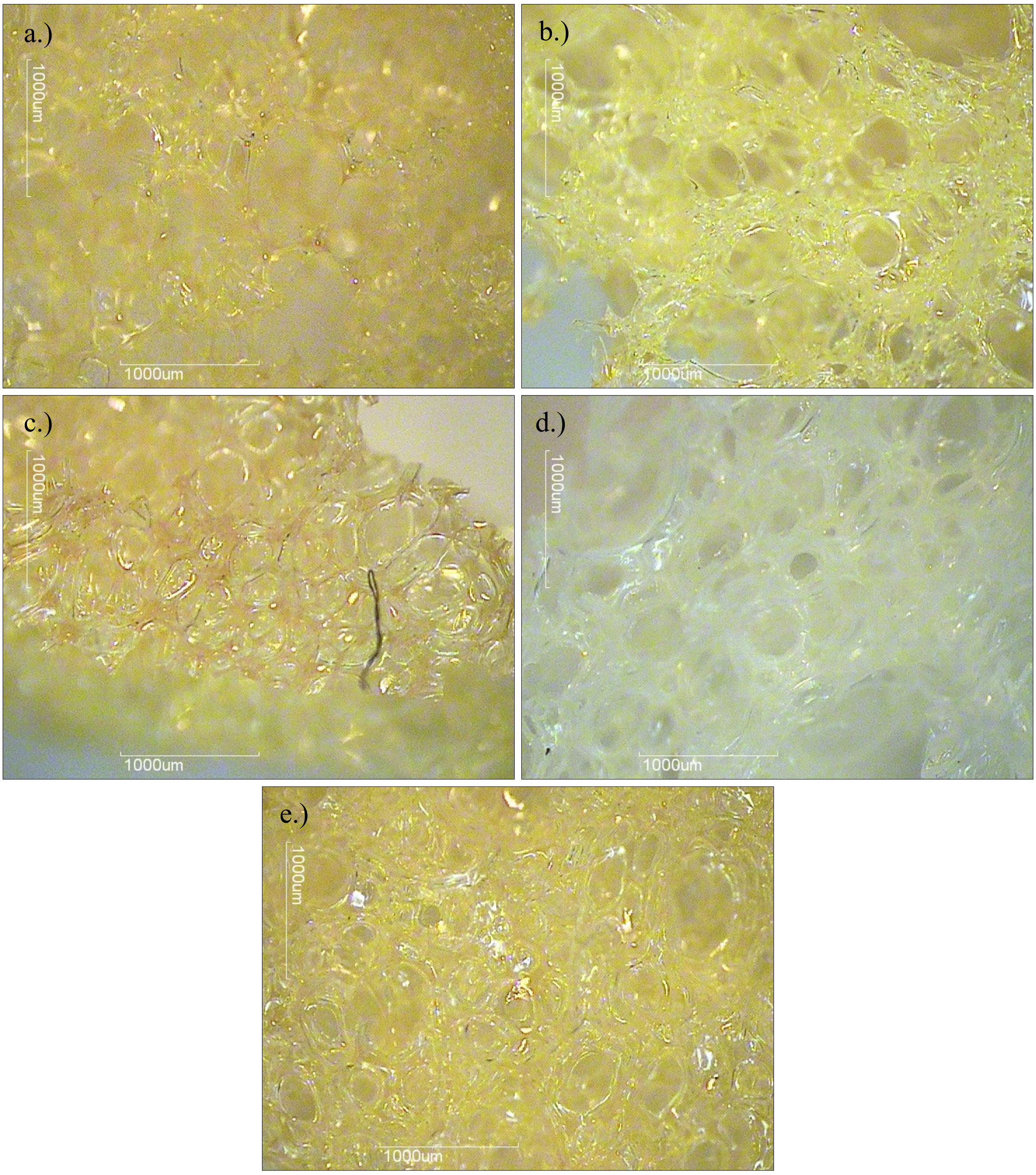

Figure S5: Micrographs of a.) non-poled sample, b.) 150 V, c.) 500 V, d.) 1051 V, and 2000 V poled samples.

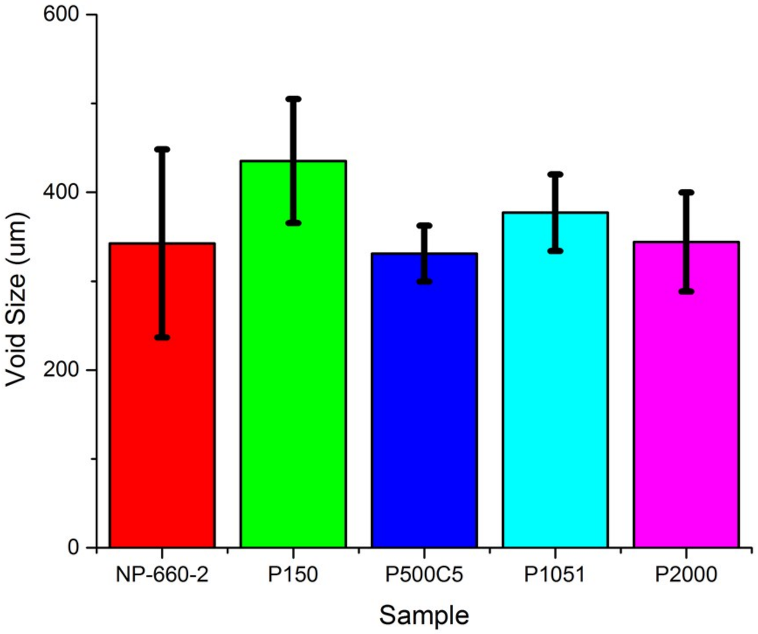

Figure S6: Average void size with error of samples above. NP – non-poled and P is poled.

Other Testing Methods

In principle, it would also be possible to measure the converse piezoelectric effect mechanically. This would, however, be experimentally challenge. For an applied voltage up to 200 V, the deformation from a material with d_{33} = 250 pC N^{-1} would be 50 nm. For a sample with a cross section of 1 cm^2 and a thickness of 5 mm, the effective spring constant would be 11 kN m^{-1} and the force for this deformation would be 0.56 mN. Such deflections would be better measured by laser interferometry.

Supporting References

[S1] A. T. McPhail, G. A. Sim, *J. Chem. Soc.* **1965**, 227 (1965).
[S2] Cambridge Structural Database
[S3] N. Tekin, M. Cebe, Ç. Tarımcı, *Chem. Phys.* **2004**, *300*, 239.