Sample Preparation and Measurement Details

Polystyrene (PS) with molecular weight \( M_w = 101.3 \text{ kg/mol} \) and \( M_w/M_n = 1.04 \) (Scientific Polymer Products) was used for the matrix (neat) PS. Pyrene-labeled polystyrene (designated PS\(^*\)) with \( M_w = 86.8 \text{ kg/mol} \) and \( M_w/M_n = 1.65 \), containing a label content of 1.93 mol%, was synthesized by free radical polymerization from styrene in the presence of trace levels of 1-pyrenylmethyl methacrylate monomer (purchased from Polysciences), as described in our previous work.\(^1,2\) Fluorophore label content was measured using UV-visible absorbance spectroscopy in high-performance liquid chromatography (HPLC) grade tetrahydrofuran (THF). Poly(vinyl methyl ether) (PVME) was purchased from Scientific Polymer Products and washed prior to use by dissolving in toluene and reprecipitating into heptane, repeated nine times. The resulting PVME used had a molecular weight of \( M_w = 80 \text{ kg/mol} \) and \( M_w/M_n = 2.5 \), as determined by gel permeation chromatography (GPC) measured with THF as eluent relative to PS standards, as reported in our previous work.\(^1\) PVME molecular weight values were determined using universal calibration with Mark-Houwink parameters \( a = 0.739 \) and \( k = 13.5 \times 10^{-3} \text{ mL/g} \).\(^3\)

Polymer blend compositions of 50/50 PS/PVME were prepared by dissolving 40% PS, 10% PS\(^*\), and 50% PVME in toluene to make solutions containing 18 wt% total polymer content. These solutions were then cast on a glass dish with flat bottom and dried in a fume hood at room temperature for 24 h, followed by annealing in a vacuum oven at 80 °C for at least 24 h to remove residual solvent. Disks of the polymer blend where then cut and used to fill a 5/8" diameter hole within a 24 µm thick Kapton sheet used as a spacer to define the electrode spacing between two transparent, conducting indium tin oxide (ITO) coated quartz substrates (1"×1" in
Electrical wires were attached with silver paste to the corners of the ITO contacts to make connection to a DC Agilent Technologies N5752A high-voltage power supply. The assembled samples, containing a final dye content <0.2 mol%, were placed under vacuum at 80 °C and pressed together with a 2.2 kg weight for 3-5 days, until the polymer blend filled in the form of the Kapton spacer. The thickness of each sample was measured to within ± 2 µm using an optical microscope (Leica DMI8 inverted microscope) by focusing on the top and bottom of the optically transparent samples and recording the displacement of the micrometer scale.

Electric field strengths up to $1.8 \times 10^7$ V/m were achieved by applying up to 440 V$_{DC}$. A schematic of our sample geometry was published in our previous work.$^1$

Steady-state fluorescence measurements were carried out using a Photon Technology International QuantaMaster fluorimeter with the sample mounted in an Instec HCS402 heat stage with liquid-nitrogen cooling capability, where the sample temperature was controlled to within ± 0.3 K. Following our previous work,$^2$ measurements of the phase separation temperature $T_S$ were done by heating the sample at a rate of 1 °C/min and monitoring the fluorescence intensity for a large increase in intensity signifying a strong reduction in fluorescence quenching occurring when the pyrene dye covalently bonded to the PS component phase separated from the more polar PVME and segregated in predominantly non-polar PS domains. The pyrene dye was excited at a wavelength of 324 nm with 4.00 nm bandpass and the resulting fluorescence monitored for 3 s every 30 s at an emission wavelength of 379 nm with 4.25 nm bandpass. Temperature jumps up and down from the one-phase to two-phase regions were done at a rate of ≈30 °C/min while the fluorescence was monitored every 15 s. In our previous work, we demonstrated that PS/PVME blends can be phase separated and subsequently remixed over and over again, while repeatedly measuring the same phase separation temperature $T_S$ value.$^1$

Typically remixing is carried out by holding the blend at 94 °C for 2 hours. Using this method, we determined an average reproducible $T_S(E=0) = 99.4 \pm 1.9$ °C across five different samples. Slight differences in $T_S(E=0)$ from sample-to-sample variability are accommodated by plotting data from each sample relative to its measured $T_S(E=0)$. After finding reproducible $T_S(E=0)$ values for each sample, measurements were continued with temperature and electric field jumps.

Figure S1 demonstrates the data collection procedure to measure the remixing time scale $\tau$ from a temperature jump. For the sample shown, the blend starts in an equilibrium, well-mixed state within the one-phase region at an initial temperature of 94 °C, 5.8 °C below its $T_S(E=0) =$
A temperature jump is then made to 104 °C, 4.2 °C above the $T_S(E=0)$, into the two-phase region and allowed to phase separate for 5 min. After 5 min, the temperature is jumped back down to the desired remixing temperature, in this case 94 °C. The black curve shown in Fig. S1a corresponds to the temperature profile assigned to the temperature controller (MK1000 High Precision Temperature Controller), while the red curve shows the measured temperature of the sample chamber recorded using the associated WinTemp software. Fig. S1b graphs the measured response of the fluorescence intensity $I(t)$ measured as a function of time through the temperature jump profile. We frequently find there is a small linear background drift of the intensity with time that we subtract off by making a linear fit to the data before and after the temperature jump, shown as a blue fit line in Fig. S1b. This gives us the intensity profile $I^*(t)$ shown in Fig. S1c, where the small linear background has been subtracted, allowing us to focus on the fluorescence intensity changes associated with the temperature jump profile. During the up jump in temperature, we notice a brief downward spike in fluorescence intensity right after the temperature is raised from 94 °C to 104 °C (from A to B) associated with fluorescence intensity generally decreasing with increasing temperature, prior to the onset of phase separation marked by the large increase in fluorescence intensity. Phase separation is allowed to proceed for 5 min at 104 °C before performing a second temperature jump back down to 94 °C. At long times the fluorescence intensity $I^*(t)$ in Fig. S1c is observed to return the same initial baseline value at 94 °C. We have quenched samples that have been phase separated for 5 min at 104 °C down to room temperature for inspection using optical microscopy finding uniformly sized domains typically smaller than ~1 µm, consistent with the reports by Halary et al. that fluorescence is sensitive to the early stages of phase separation. The fluorescence method we employ using pyrene is equivalent to that developed by Halary et al. using anthracene. Our previous work established that pyrene gives equivalent $T_S$ values to that measured by anthracene, but has the added benefit of having a higher quantum yield. Previous effort by Halary et al. also demonstrated that this fluorescence method provides equivalent phase separation temperature values to that measured by small angle neutron scattering (SANS), confirming that fluorescence is sensitive to the early stages of phase separation.

Following the temperature jump back down to 94 °C, the fluorescence intensity in Fig. S1c is observed to decay exponentially, consistent with previous reports demonstrating remixing in PS/PVME blends. We fit this data to a single exponential decay by doing a linear fit to
\[ \ln(I^*) = -\frac{t}{\tau} + \ln(I_0) \] as depicted in Fig. 1Sd, where \( t = 0 \) is defined as when the measured sample temperature has stabilized at the remixing temperature (point D). Fits are extended until the data fall to within the noise level of the intensity data. This experiment was repeated on both nominally identical samples and on the same sample where complete remixing of the blend is done by holding the sample for 2 h at 94 °C, as demonstrated in our previous work. \(^1\) Figure S2 graphs the fluorescence intensity decay \( \ln(I^*) \) vs time for samples remixed at 90 °C and 85 °C, without (a) and with (b) an applied electric field of \( E = 1.28 \times 10^7 \) V/m. The measured remixing time scales for these samples are (a) \( \tau(90 \, ^\circ \text{C}) = 440 \) s and \( \tau(85 \, ^\circ \text{C}) = 1600 \) s under zero field, and (b) \( \tau(90 \, ^\circ \text{C}) = 420 \) s and \( \tau(85 \, ^\circ \text{C}) = 1550 \) s under an electric field of \( E = 1.28 \times 10^7 \) V/m, representing some of the \( \tau(T) \) data plotted in Figure 3 of the main text.

**Figure S1.** Fluorescence intensity data collection procedure during a temperature jump. (a) Temperature jump profile applied (black) and measured (red) to the sample starting in
equilibrium within the one-phase region at 94 °C, jumping up to 104 °C to allow the blend to phase separate for 5 min, followed by a temperature jump back down to 94 °C. (b) Raw measured fluorescence intensity during the temperature jump, along with a straight line fit (blue line) used to subtract the small linear background drift. (c) Time dependence of the fluorescence intensity profile $I^*(t)$, measured intensity with small linear background drift subtracted, demonstrating the sharp increase in fluorescence intensity during phase separation followed by the exponential decay during remixing. (d) Semi-log plot used to determine the remixing time scale $\tau$.

Figure S2. Time-dependence of the fluorescence intensity decay plotted as $\ln(I^*)$ vs. time $t$ for 50/50 PS/PVME blends remixed at 90 °C and 85 °C without (a) and with (b) an applied electric field of $E = 1.28 \times 10^7$ V/m. Green lines show fits to a single exponential decay: $\ln(I^*) = -t/\tau + \ln(I_0)$. 
References

(1) Kriisa, A.; Roth, C. B. Electric Fields Enhance Miscibility of Polystyrene/Poly(vinyl methyl ether) Blends. *J Chem Phys* **2014**, *141*, 134908.

(2) Kriisa, A.; Park, S. S.; Roth, C. B. Characterization of Phase Separation of Polystyrene/Poly(vinyl methyl ether) blends Using Fluorescence. *J Polym Sci, Part B: Polym Phys* **2012**, *50*, 250–256.

(3) Bauer, B. J.; Hanley, B.; Muroga, Y. Synthesis and Characterization of Poly(vinyl methyl ether). *Polym Commun* **1989**, *30*, 19–21.

(4) Halary, J. L.; Ubrich, J. M.; Monnerie, L.; Yang, H.; Stein, R. S. Isotope Effects on the Phase Separation in Polystyrene-Poly(vinyl methyl ether) Blends. *Polym Commun* **1985**, *26*, 73–76.

(5) Halary, J. L.; Ubrich, J. M.; Nunzi, J. M.; Monnerie, L.; Stein, R. S. Phase Separation in Polystyrene-Poly(vinyl methyl ether) Blends: a Fluorescence Emission Analysis. *Polymer* **1984**, *25*, 956–962.

(6) Larbi, F. B.; Halary, J. L.; Monnerie, L. Kinetics of Phase Separation in Binary Mixtures of Polystyrene and Poly(vinyl methyl ether) as Studied by Fluorescence Emission of Labeled Polystyrene. *Macromolecules* **1991**, *24*, 867–871.

(7) Feng, Y.; Han, C. C.; Takenaka, M.; Hashimoto, T. Molecular Weight Dependence of Mobility in Polymer Blends. *Polymer* **1992**, *33*, 2729–2739.