

Supporting Information

Stereoregulation, molecular weight, and dispersity control of PMMA synthesized via free-radical polymerization supported by the external high electric field.

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1. EXPERIMENTAL SECTION

Materials.

Methyl methacrylate (MMA, >99%, Sigma Aldrich) was dried over molecular sieves and stored in a freezer under nitrogen. 2,2'-Azobis(2-methylpropionitrile) (AIBN, 98%, Sigma-Aldrich), methanol (98%, Chempur), chloroform (98.5%, Chempur), chloroform-d (Sigma Aldrich) were used as received.

Instruments.

^1H and ^{13}C NMR spectra were collected on Bruker Ascend 500 MHz spectrometer for the samples in DMSO, CDCl_3 at 25 °C. Molecular weights (M_n) and dispersity (D) of produced polymers were determined by Size Exclusion Chromatography (SEC) with a Viscotec GPC Max VR 2001 and a Viscotec TDA 305 triple detection containing refractometer, viscosimeter, and low angle laser light scattering. The OmniSec 5.12 was used for data processing. Two D6000M (General Mixed Org 300x8mm) and Dguard (Org Guard Col 10x4.6mm) columns were used for separation. The measurements were carried out in DMF with LiBr (10 mmol) as the solvent at 40 °C with a flow rate of 0.7 mL/min.

Procedures.

We have carried out the free radical polymerization of the methyl methacrylate (MMA) using 2,2'-Azobis (2-methylpropionitrile) (AIBN) as an initiator. To prepare a reaction mixture MMA and AIBN (0.5 wt% in respect to MMA) were added to a Schlenk flask with a magnetic stirring bar and degassed by three freeze-pump-thaw cycles. Next, the prepared mixture was transferred to a sample cell (~ 1ml) and mounted inside the nitrogen gas cryostat (Novocool Quatro System). The temperature was immediately increased to $T= 333$ K, which was selected as polymerization temperature. After a predetermined polymerization time, the recovered material was removed from the capacitor using chloroform-*d*, then evaporated and dissolved in cold methanol. The final polymer sample was dried under vacuum to a constant mass, yielding 0.50-0.95 mg pure PMMA. ^1H NMR [400MHz, CDCl_3] $\delta=0.64$ -1.22 (3H: methyl group), 1.74-1.9 (2H: methylene protons of PMMA main chain), 3.53 (3H, methoxy groups of PMMA).

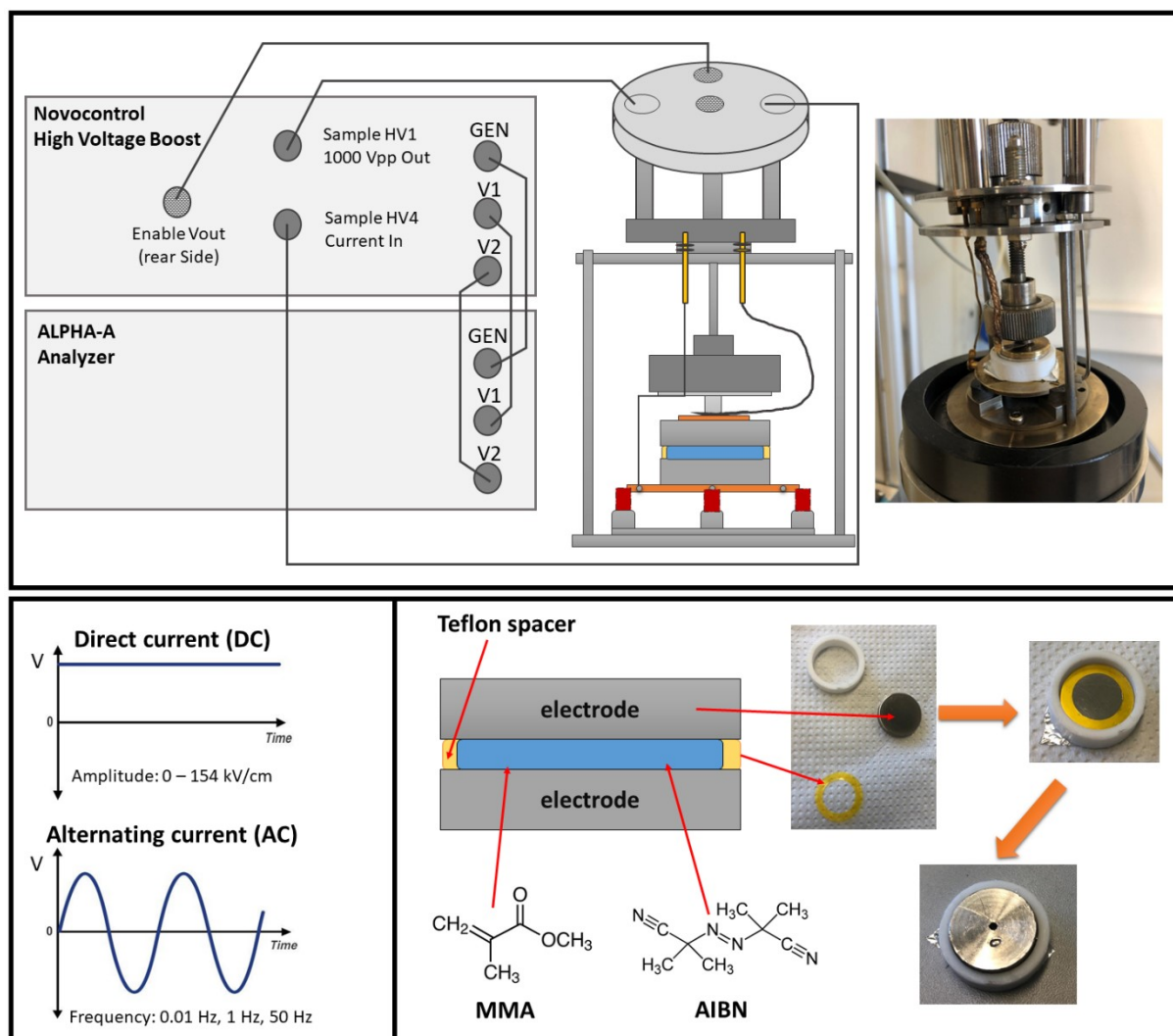
High-field conditions.

At low fields, the applied voltage across the sample of micrometer thickness is often not more than 10 V. In such cases, polarization P and field E is proportional to each other; this is a linear response regime. When operating within a linear response regime, the applied electrical field does not significantly modify the molecular dynamics of the studied system. However, when going much beyond 10 kV/cm, the relation between the polarization of the sample and the external electric field is not linear anymore. Under such conditions, the external electric field forces a parallel dipole alignment and changes the relative orientation of the molecules. Much energy is also irreversibly transferred from the electric field to the sample. As a result, the molecular system exposed to high electric fields reveals significant changes in dynamics and thermodynamics.¹⁻³ Thus, when the field is switched off, the system may not come back to the initial state. In principle, each molecular system with a non-zero molecular dipole moment can be brought into such a state. It is only a matter of the field intensity, high enough to produce the desired effect. Since $E=V/d$, high fields are generated by increasing the voltage applied, reducing the sample thickness, or either both. Voltages are applied in static ($\nu=0$ Hz), or alternating ($\nu \neq 0$ Hz) current conditions. In contrast to DC bias fields, the AC field amplitude changes sinusoidally with non-zero frequency. The use of low-frequency AC fields can be equated with static fields.

Dielectric spectroscopy (DS).

High-field polymerization was carried out under isothermal conditions ($T= 333$ K) for 12 hours. The reaction mixture was kept between two parallel plate electrodes, forming a sandwich-like capacitor. Flat and highly-polished electrode surfaces are required to maintain a homogenous field. Under such conditions, the field lines are parallel, and the electric field properties are precisely defined and controlled. Electrodes (20 mm in diameter) were separated by 19.5 μm thick Teflon ring spacer. The sandwich-like capacitor was mounted in the dielectric sample cell and placed inside a nitrogen gas cryostat. The high-voltage was applied to the sample using a high-voltage source “HVB1000” from Novocontrol (for details https://www.novocontrol.de/php/ti_hvb1000.php). The HVB 1000 extension allows to reach dc and/or ac voltages up to ± 500 V (peak voltage). In combination with a frequency-response analyzer Alpha Analyzer (Novocontrol, for details https://www.novocontrol.de/php/ana_alpha.php), it is possible to probe simultaneously the

dielectric response of the sample exposed to high electric fields. In this configuration, the available frequency range is from mHz to 10 kHz. [Scheme S1](#) demonstrates the experimental setup.



[Scheme S1](#). Scheme of the experimental setup used in this study.

The system was maintained at $T = 333$ K. The temperature stability within 0.1 K was ensured using a Novocontrol Quatro system (for details https://www.novocontrol.de/php/temp_contr_qpop.php). The electric field was switched on immediately after reaching 333 K and switched off after 12 h. As the concentration of monomer units and the dipole moment distribution of the sample change with reaction progress, the polymerization kinetics can be followed by dielectric spectroscopy. For that, we use a low-

amplitude sinusoidal field ($E < 1$ kV/cm), while on top of that high electric field is applied ($E \gg 10$ kV/cm). In this way, the evolution of the real (ϵ') and imaginary (ϵ'') parts of complex permittivity, $\epsilon^* = \epsilon' - i\epsilon''$ provides information about changes in the behavior of the examined material exposed to a high electric field in the real-time of the experiment. After completing polymerization, the electric field was switched off. The reaction was assumed to be completed when no further changes in the dielectric spectra were observed. The reaction mixture solidified due to polymerization, both in the absence and presence of a static electric field. Then, the sample was removed from the capacitor for further characterization. In the present study, we use DC electric fields of various field magnitudes (26 kV/cm, 77 kV/cm, 104 kV/cm, 154 kV/cm) as well as an AC electric field with a magnitude of 77 kV/cm while different frequencies (0.01 Hz, 1 Hz, and 50 Hz). Experiments at zero DC field were also performed as a reference. The field amplitudes are reported as root-mean-square (RMS) values.

Dielectric spectroscopy (Alpha Analyzer with Novocool temperature control system, Novocontrol) was also employed to characterize the segmental dynamics of isolated PMMA samples obtained at high electric fields. Before that, the polymers were purified from the remaining contaminants. This experiment also uses a parallel plate capacitor (10 mm in diameter) separated by a Teflon spacer of the same thickness, just as before. Measurements within a low-field regime were carried out in the temperature range from 256 K - 413 K. Dielectric spectra for isothermal polymerization measurements were collected within the frequency range of 1 Hz to 10 kHz, and those for non-isothermal measurements are within 0.05 Hz to 10^6 Hz.

DSC measurements.

Thermodynamic properties of isolated and dried PMMA polymers obtained under electric fields were studied using a Mettler-Toledo DSC 1STARe System. The instrument has an HSS8 ceramic sensor with 120 thermocouples and a liquid nitrogen cooling station. Zinc and indium standards were used to calibrate the devices before the measurements. Samples were sealed in aluminum crucibles (40 μ L) and measured on heating from 273 K to 453 K at a constant heating rate of 10 K/min. Each measurement at a given temperature was repeated three times. The glass transition temperatures T_g are obtained from midpoints of the heat capacity increments.

2. ADDITIONAL RESULTS

Control experiments

We have carried out solvent-assisted reactions (utilizing anisole as a solvent) in the presence and absence of a high DC bias at 333 K (60°C). Solvent reactions were conducted with 50 wt% of anisole with respect to MMA. In both cases, MMA conversions reached >99%. In the absence of a high electric field, we observe a similar trend to bulk polymerization. The reaction is poorly controlled and yields to PMMA with higher M_n and higher \bar{D} (Table S1). Remarkably, at a high electric field, PMMA produced in the presence of anisole as a solvent was characterized by a higher content of isotactic fraction compared to zero-field reference but still lower than those noticed for bulk processes.

Table S1. Control experiments for high electric field-assisted MMA FRP (bulk vs. solvent polymerization).

Conditions	Conv [%] ^a	$M_{nSEC-LALLS}$ [g/mol] ^b	M_w/M_n ^b	mm ^a	mr ^a	rr ^a
MMA+AIBN+ 0 kV/cm at 333 K	>99	916 900	1.90	11.5	29.5	59
MMA+AIBN+0 kV/cm+anisole at 333 K	>99	558 000	2.765	13.2	28.9	57.9
MMA+AIBN+ 154 kV/cm (DC) at 333 K	>99	402 388	1.65	57.3	12.9	29.8
MMA+AIBN+154 kV/cm (DC)+anisole at 333 K	>99	307 000	1.778	31.1	23.7	45.2

^adetermined by ¹H NMR, ^bdetermined by SEC-LALLS (DMF+10 mmol LiBr); bulk reactions were conducted with 0.5 wt% of AIBN in respect to MMA; solvent reactions were conducted with 50 wt% of anisole in respect to MMA.

Unfortunately, due to a very small amount of the sample, we were not able to perform a detailed analysis and characterize obtained product at a very low conversion regime (SEC analysis was not possible). We have performed an additional analysis of the product recovered after 1.5h. As expected, we found that the monomer conversion, molecular weight, and dispersity of the produced polymer were similar to the product recovered after 12 h (Table S2). This is a typical feature of free radical polymerization, where high monomer conversion and molecular weight are achieved very quickly. Therefore one could hypothesize that the application of the high electric field does not change the character of FRP. However, this claim must be verified by carrying additional reactions at much shorter reaction times at a low monomer conversion regime. Currently, we are not able to perform such experiments since this requires redesigning and reconstructing our setup dedicated to measuring a small amount of the sample. Nevertheless, our

results clearly indicate that applying the high electric field allows us to significantly reduce M_n , dispersity, and change the microstructure of the obtained polymers.

Table S2. Control experiments for high electric field-assisted MMA FRP (shortening polymerization time).

Conditions	Conv [%] ^a	$M_n^{\text{SEC-LALLS}}$ [g/mol] ^b	M_w/M_n^b	mm ^a	mr ^a	rr ^a
MMA+AIBN+ 0 kV/cm at 333 K	>99	916 900	1.90	11.5	29.5	59
MMA+AIBN+ 0 kV/cm at 333 K (reaction stopped after ~ 1.5h)	98	Not possible	Not possible	11.1	27.2	61.7
MMA+AIBN+ 154 kV/cm (DC) at 333 K	>99	402 388	1.65	57.3	12.9	29.8
MMA+AIBN+ 154 kV/cm at 333 K (reaction stopped after ~ 1.5h)	94	Not possible	Not possible	43.4	23.2	33.4

^adetermined by ¹H NMR, ^bdetermined by SEC-LALLS (DMF+10 mmol LiBr); bulk reactions were conducted with 0.5 wt% of AIBN in respect to MMA.

Table S3. Control experiments for high electric field-assisted MMA FRP (AIBN decomposition).

Conditions	Conv [%] ^a	$M_n^{\text{SEC-LALLS}}$ [g/mol] ^b	M_w/M_n^b	mm ^a	mr ^a	rr ^a
MMA+154 kV/cm DC at 333 K	0	-	-	-	-	-
MMA+154 kV/cm DC at 298 K	0	-	-	-	-	-
MMA+AIBN+154 kV/cm DC at 298 K	8	-	-	-	-	-
MMA+AIBN+0 kV/cm at 298 K	0	-	-	-	-	-
MMA+AIBN+ 0 kV/cm at 333 K	>99	916 900	1.90	11.5	29.5	59
MMA+AIBN+ 154 kV/cm (DC) at 333 K	>99	402 388	1.65	57.3	12.9	29.8

^adetermined by ¹H NMR, ^bdetermined by SEC-LALLS (DMF+10 mmol LiBr); bulk reactions were conducted with 0.5 wt% of AIBN in respect to MMA.

In the absence of AIBN, polymerization has not occurred at both 298 K and 333 K (Table S3). The presence of radicals is needed to trigger MMA polymerization. Surprisingly, the experiment performed at 298 K gave 8% MMA consumption (MMA+0.5 wt% of AIBN). However, due to a minimal quantity of resulting PMMA samples, its SEC-LALLS characteristic was impossible. Nevertheless, this experiment clearly showed that a high electric field could be another external factor - as 2D hard confinement previously reported by some of us⁴ - allowing for AIBN decomposition below its typical temperature range 323 K-343 K.

NMR spectra and SEC chromatograms for PMMA samples obtained upon polymerization carried out in the presence of high electric fields

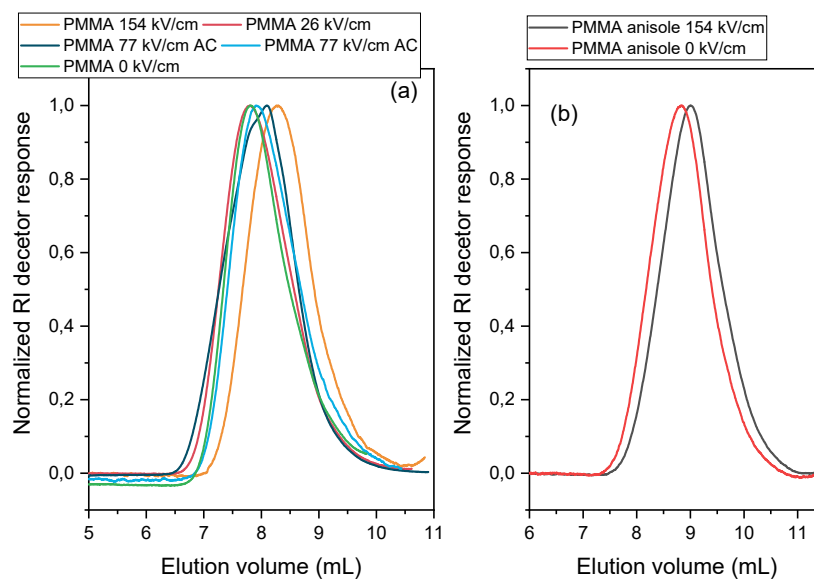


Figure S1. SEC-LALLS traces of PMMAs prepared *via* thermally-induced FRP under different e-fields (DMF+10 mmol LiBr) (a) without the solvent and (b) in the presence of anisole as a solvent

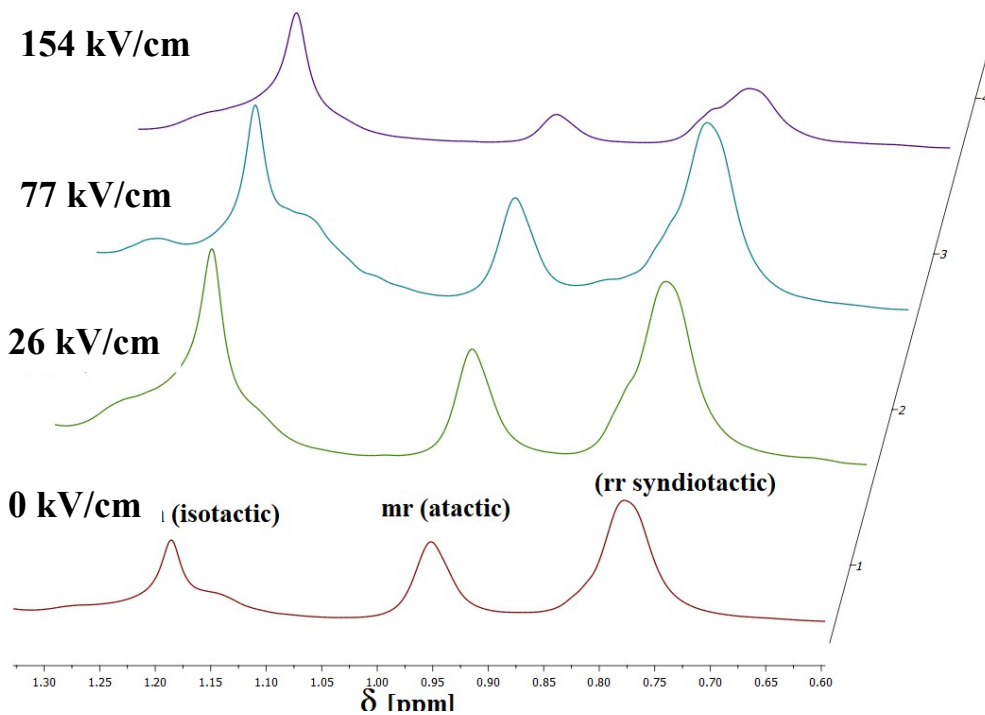


Figure S2. ^1H NMR spectra of $\alpha\text{-CH}_3$ of PMMA in CDCl_3 for PMMA synthesized at FRP under different electrical field

The glass transition dynamics of PMMA produced at high electric fields.

Next, we have investigated the glass transition dynamics of produced PMMA samples. Dielectric measurements were carried out for three samples obtained at high DC fields: 0 kV/cm, 77 kV/cm, and 154 kV/cm. Dielectric spectra were collected on cooling within the temperature range of 256 - 413 K. [Figure S3a](#) presents the representative dielectric loss spectra for PMMA produced in the presence of a DC electric field of $E = 77$ kV/cm. Two relaxation processes were observed in the dielectric loss spectra. Slower α -relaxation is associated with segmental mobility and a faster secondary process, JG β -relaxation.⁵⁻⁸ The exact origin of the β -relaxation in PMMA was discussed in our previous work.⁹ It is worth mentioning that both processes were difficult to distinguish because the β -relaxation in PMMA is more intense than the segmental relaxation. The lower intensity of the segmental relaxation for syndiotactic and atactic PMMA was also reported in the literature.^{8,10,11}

To get more details on the relaxation dynamics, dielectric data were fitted using the Havriliak–Negami (HN) function¹²

$$\varepsilon^*(\omega) = \varepsilon_{\infty} + \frac{\Delta\varepsilon}{\left[1 + (i\omega\tau_{HN})^{\alpha_{HN}}\right]^{\gamma_{HN}}} \quad (1)$$

where ε_{∞} is the high-frequency limit permittivity, $\Delta\varepsilon$ is the relaxation strength, τ_{HN} is the relaxation time, α_{HN} and γ_{HN} are the parameters characterizing the shape of the dielectric loss curve, while ω is the angular frequency ($\omega = 2\pi f$). The dielectric loss spectra measured for the obtained PMMA samples were fitted by the superposition of the two HN functions and the DC conductivity. In [Figure S3b](#), we demonstrate representative fits of the HN functions to the raw data for PMMA obtained in the presence of a DC field of $E = 77$ kV/cm.

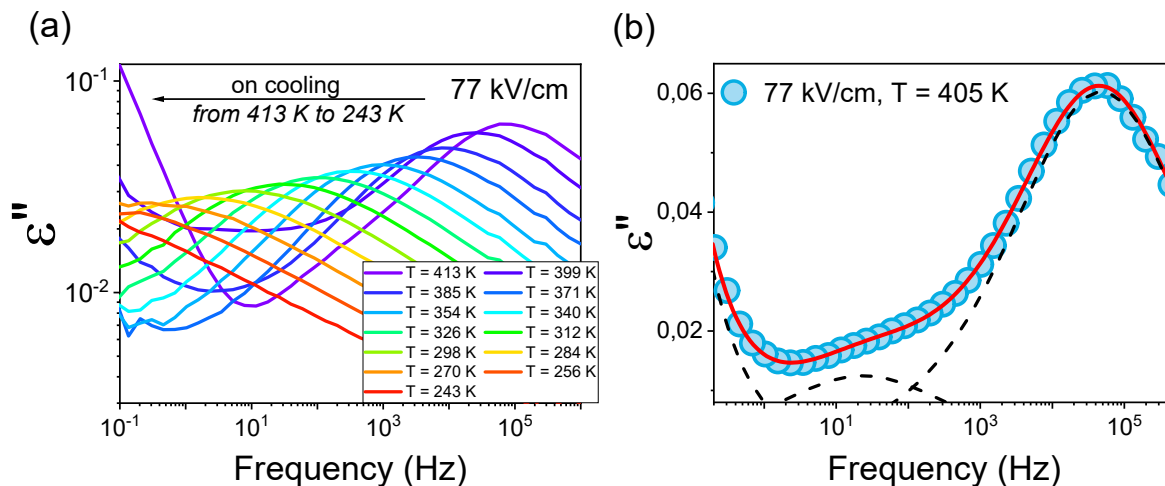


Figure S3. (a) Dielectric loss spectra measured at different temperatures for PMMA synthesized during polymerization under the DC field of $E = 77$ kV/cm. Data were collected on slow cooling (~ 0.3 K/min). (b) Selected dielectric loss spectrum obtained for PMMA at the temperature $T = 405$ K. The tested polymer was synthesized by applying the DC field of $E = 77$ kV/cm during polymerization. The solid lines are fits of the entire spectrum according to the superposition of the two Havriliak-Negami functions and DC conductivity.

Figure S4 shows the temperature dependences of the segmental and secondary relaxation times for three PMMA samples obtained in the absence and presence of high electric field E (77 kV/cm and 154 kV/cm). Due to the significant overlapping of the α - and β -relaxation, it was not possible to determine the segmental relaxation times from the entire range of the measured temperatures. As demonstrated, the segmental dynamics of PMMA polymers obtained at high fields are faster compared to the sample synthesized at no electric field. Moreover, our results indicate that segmental dynamics are enhanced when the field magnitude increases upon polymerization. On the other hand, we have noticed that the temperature dependence of the secondary relaxation times is the same for all samples.

It is well-known that the glass transition temperature depends strongly on the polymer molecular weight. Namely, in the range of low molecular weights, T_g changes almost linearly with M_n , while it is independent of the molecular weight above a certain threshold value. For PMMA,

the literature data defines such a point for $M_n > 11\,000$ g/mol.^{13–15} Therefore, changes in the segmental dynamics observed for PMMA samples produced at high electric fields cannot be related to the molecular weight differences. This effect comes from the differences in the fraction of isotactic, syndiotactic, and atactic triads. The influence of molecular order on the glass transition dynamics of PMMA is known from the literature.^{5,9,16}

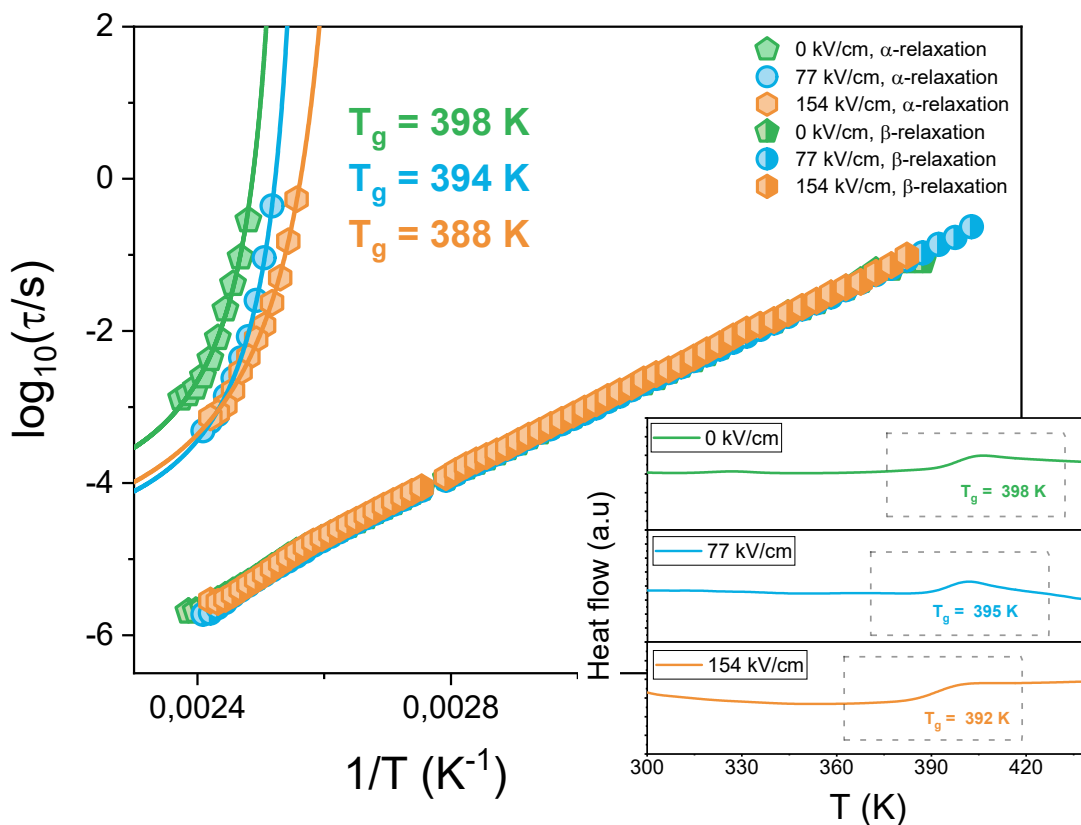


Figure S4. (a) The α - and β -relaxation time plotted as a function of the inverse temperature for PMMA samples obtained by polymerization at zero-field and high DC fields (77 kV/cm, 154 kV/cm). The solid lines are the fitting of the data to the VFT equation. The inset shows DSC thermograms for PMMA samples produced by free-radical polymerization carried out at high electric fields.

The temperature dependences of the α -relaxation times for three measured samples (0 kV/cm, 77 kV/cm, 154 kV/cm) were fitted with Vogel-Fulcher-Tammann (VFT) equation.^{17–19}

$$\tau_{\alpha} = \tau_{\infty} \exp\left(\frac{D_T T_0}{T - T_D}\right) \quad (2)$$

where τ_{∞} is the relaxation time, T_0 is the temperature at which τ_{α} goes to infinity, and D_T is the fragility parameter. Based on dielectric data, we have defined T_g for all tested PMMA samples as a T at which $\tau_{\alpha} = 10^2$ s. The glass transition temperature of the sample synthesized at zero-field is 398 K. For the samples obtained in the presence of the DC field with 77 kV/cm and 154 kV/cm, the calculated T_g^S are 394 K and 386 K, respectively. They are in good agreement with the corresponding calorimetric values. The DSC thermograms are shown in [Figure S4](#). An endothermic event seen on DSC scans is related to the vitrification process. Thus, the results demonstrate that increasing the field amplitude upon high-field polymerization decreases the glass transition temperature of the obtained polymer. Herein, the spatial configuration is the main factor influencing the glassy dynamics of produced PMMA samples.

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