Supporting Information Section

Origin of the α-, β-, (αβ)-, and "slow" dielectric processes in poly(ethyl methacrylate).
K. Mpoukouvalas, G. Floudas* and G. Williams*

A. Derivation of the expressions for the ratio $\Re$ of the constant volume and constant pressure apparent activation energies

<u>Case 1. $W = Y, X \neq Z$</u>
e.g. *VP*/*VT*, Eq.(6) of the text, is obtained as follows.

We start by writing τ=τ(*T*, *V*), τ=τ(*T*, *P*) with *V*=*V*(*T*, *P*) giving

$$(\partial \ln \tau / \partial V)_P = (\partial \ln \tau / \partial T)_V (\partial T / \partial V)_P + (\partial \ln \tau / \partial V)_T \quad \text{(S.1)}$$

$$(\partial \ln \tau / \partial T)_P = (\partial \ln \tau / \partial T)_V + (\partial \ln \tau / \partial V)_T (\partial V / \partial T)_P \quad \text{(S.2)}$$

hence

$$\begin{aligned} VP/VT &= (\partial \ln \tau / \partial V)_P / (\partial \ln \tau / \partial V)_T = 1 + ((\partial \ln \tau / \partial T)_V (\partial T / \partial V)_P / (\partial \log \tau / \partial V)_T) \\ &= 1 - (\partial V / \partial T)_\tau / (\partial V / \partial T)_P \end{aligned} \quad \text{(S.3)}$$

Using Eq.(S.2) to replace $(\partial \ln \tau / \partial V)_T$ on the right hand side of Eq.(S.3) gives

$$VP/VT = (1 - \Re)^{-1} \quad \text{(S.4)}$$

Eqs.(S3) and (S4) correspond to Eq.(6) of the text. Eq.(7) follows from the definition of $\Re$ while Eq.(8) is obtained by a procedure similar to that used to derive Eq.(6).

<u>Case 2. $W = Z, X = Y$</u>
e.g. *PT*/*TP* Eq.(11) is obtained by writing $\tau = \tau(T, P)$

$$(\partial \ln \tau / \partial T)_V = (\partial \ln \tau / \partial T)_P + (\partial \ln \tau / \partial P)_T (\partial P / \partial T)_V \quad \text{(S.5)}$$

$$PT/TP = [(\partial \ln\tau/\partial T)_V - (\partial \ln\tau/\partial T)_P)]/((\partial \ln\tau/\partial T)_P(\partial P/\partial T)_V)$$

$$= -(1-\Re)/(\partial P/\partial T)_V = -(\partial T/\partial P)_\tau \tag{S.6}$$

Eq.(9) and (10) of the text are obtained by a similar procedure, writing $\tau = \tau(T,V)$ and $\tau = \tau(P,V)$ respectively.

Case 3. *W = Z, X ≠ Y*

e.g. *TP/VT*, Eq.(12) is obtained from Eq.(7) and (9) as

$$(TV/VT)/(TV/TP) = (\partial V/\partial T)_P (1-\Re)^{-1} \tag{S.7}$$

In a similar manner Eq.(7) and Eq.(11) give *TV/PT* (Eq.13); Eq.(8) and (10) give *PT/VP*, Eq.(14); Eq.(8) and (11) give *PV/TP* Eq.(15); Eq.(6) and (9) give *VP/TV* (Eq.(16) while Eq.(6) and (10) give *VT/PV* (Eq.17).

Case 4. *W ≠ X, Y ≠ Z*

e.g. Eq.(18)-(20) may be confirmed as follows; e.g. for Eq.(20) using Eq.(8) and (17)

$$(PT/VT) = (PT/PV)(PV/VT) = (\partial V/\partial P)_T \tag{S.8}$$

A further set of equations of the form $\Re = (1+\lambda)^{-1}$ may be obtained from the generalized Arrhenius equation $\tau = \tau_0 \exp[Q(T,P)/RT]$. It is easy to show that

$$TP = -\frac{Q}{RT^2}[1 - T(\partial \ln Q/\partial T)_P] \quad ; \quad TV = -\frac{Q}{RT^2}[1 - T(\partial \ln Q/\partial T)_V]$$

$$PT = \frac{1}{RT}(\partial Q/\partial P)_T \quad ; \quad VT = \frac{1}{RT}(\partial Q/\partial V)_T \tag{S.9a-d}$$

From Eq.7 we write

$$\Re = TV/TP = \frac{1 - T(\partial \ln Q/\partial T)_V}{1 - T(\partial \ln Q/\partial T)_P} = \frac{A}{1+\lambda_a} \qquad \text{(S.10)}$$

where $A = 1 - T(\partial \ln Q/\partial T)_V$ and $\lambda_a = -T(\partial \ln Q/\partial T)_P$. Two further relations for $\Re$ are obtained by a similar method, giving

$$\Re = [1+\lambda_b/A]^{-1} \quad ; \quad \Re = [1+\lambda_c/A]^{-1} \qquad \text{(S.11a,b)}$$

where $\lambda_b = T(\partial \ln Q/\partial P)_T(\partial P/\partial T)_V$ and $\lambda_c = -T(\partial \ln Q/\partial V)_T(\partial V/\partial T)_P$.

For the case $Q = Q(V)$ then A = 1. Roland and coworkers proposed that $Q = Q(V) = C/V^{\gamma}$ may be applied to the α-process in glass-forming materials.[34,35] For this case $(d\ln Q/d\ln V) = -\gamma$ giving $\lambda_a = \lambda_b = \lambda_c = T\alpha_P\gamma$, so $\Re = [1+T\alpha_P\gamma]^{-1}$.

B. Further Dielectric Data

Additional dielectric loss data are provided for PEMA (M_w=2.0x10^3 g/mol) under "isothermal" conditions at 383.15 K (T>>T_g) (in Figure S1). The spectra show the separation of the αβ-process to α- and β-processes that are well resolved at elevated pressures. Figure S2, comprises the temperature normalized dielectric strengths ($T\Delta\varepsilon$) for the three processes at all temperatures investigated as a function of applied pressure. The complementary in the dielectric strengths of the α- and β-processes can be seen. In Figure S3, the experimentally obtained ratio of activation energies, obtained from the $\tau(\rho)$ representation using Eq. (6), is shown for each of the relaxation processes. This is made by coupling the relaxation times measured under "isobaric" $\tau(T)$ and "isothermal" $\tau(P)$ conditions with the equation of state $V(T,P)$.

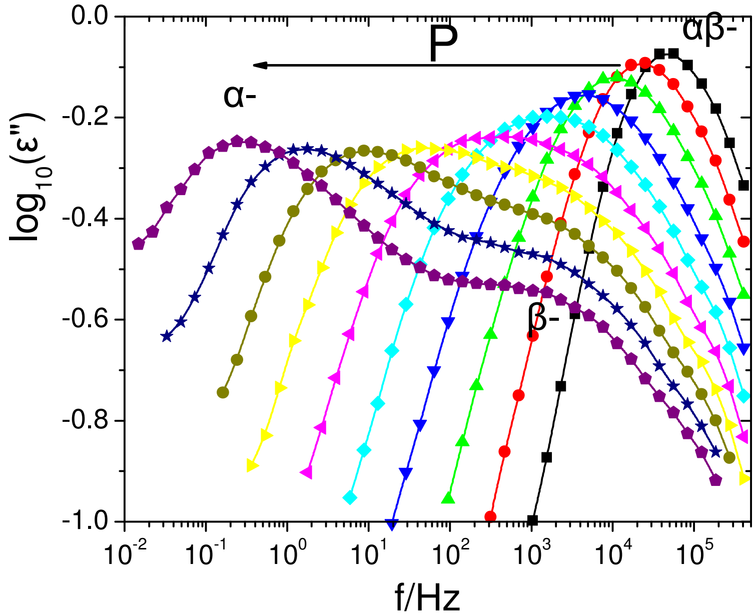

Figure S1. Dielectric loss curves for PEMA (M_w=2.0x10^3 g/mol) under "isothermal" conditions at T=383.15 K. The curves are at (squares): 0.1, (circles): 30, (up triangles): 60, (down triangles): 90, (rhombus): 120, (left triangles): 150, (right triangles): 180, (polygons): 210, (stars): 240 and (pentagons): 270 MPa.

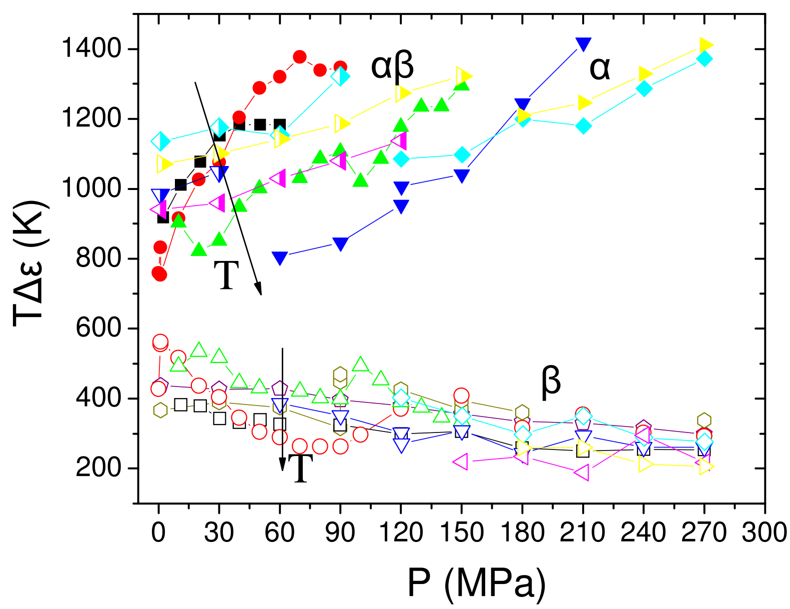

Figure S2. Pressure dependence of the dielectric strength $T\Delta\varepsilon$ of PEMA (M_w=2.0x10^3 g/mol), corresponding to the three processes as follows: β- (open symbols), α- (filled symbols) and αβ-process (half-filled symbols) at the different temperatures investigated: (pentagons): 323.15, (polygons): 333.15, (squares): 343.15, (circles): 353.15, (up triangles): 363.15, (down triangles): 373.15, (rhombus): 383.15, (left triangles): 393.15 and (right triangles): 403.15 K.

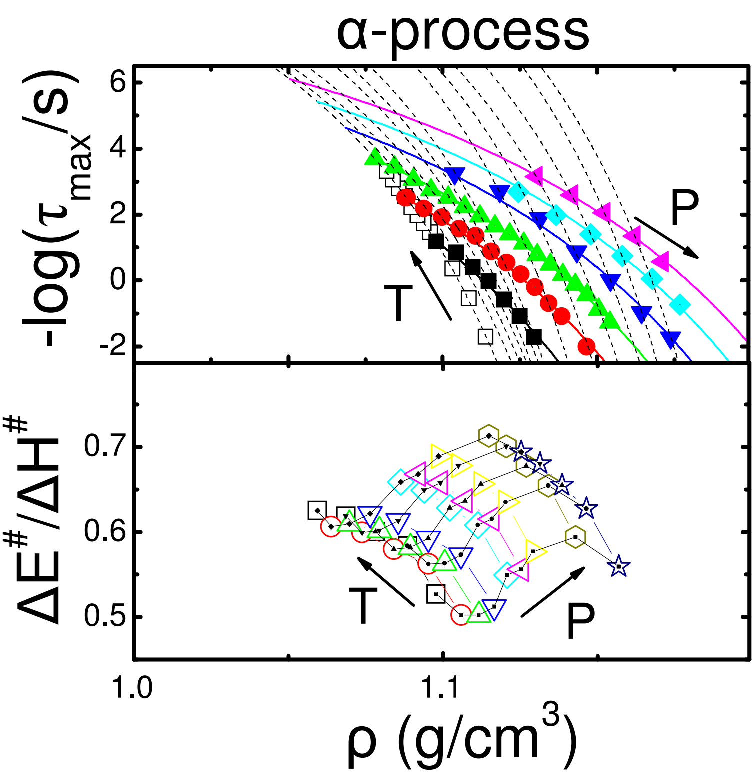

Figure S3a. (Top): Dependence of the "isothermal" (solid lines) and "isobaric" (dashed lines) relaxation times of PEMA (M_w=2.0x10^3 g/mol) on density. The "isothermal" and "isobaric" lines, are the result of the fits to the modified VFT equation (Eq. 28) to the α-process. The different "isotherms" are: (squares): 343.15, (circles): 353.15, (up triangles): 363.15, (down triangles): 373.15, (rhombus): 383.15 and (left triangles): 393.15 K. In all cases the "isobaric" data at P=0.1 MPa are shown with open squares. **(Bottom)**: Ratio $\Re$, of the constant-volume activation energy ($\Delta E^{\#}$) to the enthalpy of activation ($\Delta H^{\#}$) for the α-process plotted against density. The "isobars" are now shown with open symbols: (squares): 0.1, (circles): 10, (up triangles): 20, (down triangles): 30, (rhombus): 40, (left triangles): 50, (right triangles): 60, (polygons): 90 and (stars): 120 MPa.

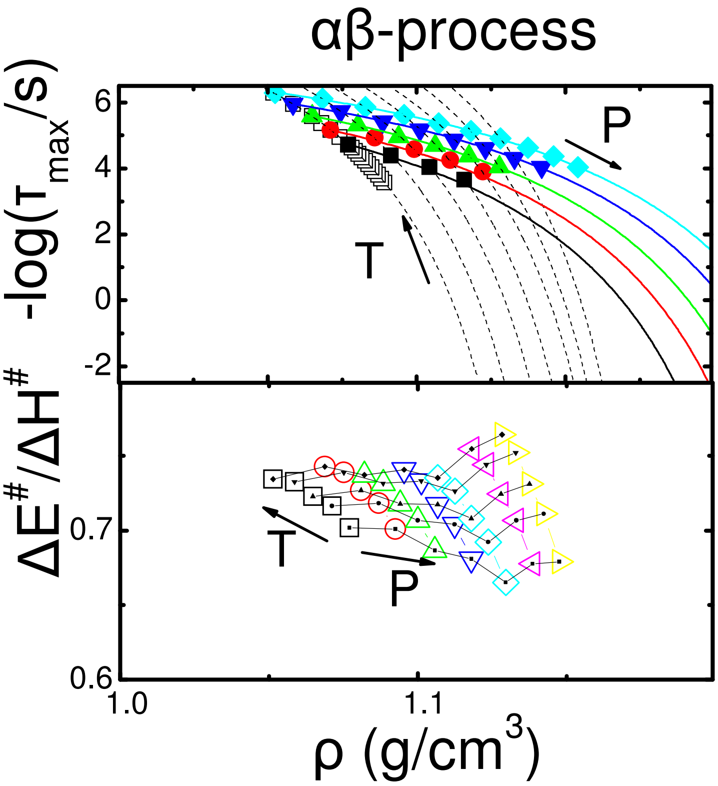

Figure S3b. (Top): Dependence of the "isothermal" (solid lines) and "isobaric" (dashed lines) relaxation times of PEMA (M_w=2.0x10^3 g/mol) on density corresponding to the (αβ)-process. The "isothermal" and "isobaric" lines, are the result of the fits to the modified VFT equation (Eq. 28). The different "isotherms" are: (squares): 383.15, (circles): 393.15, (up triangles): 403.15, (down triangles): 413.15 and (rhombus): 423.15 K. In all cases the "isobaric" data at P=0.1 MPa are shown with open squares. **(Bottom)**: Ratio $\Re$, of the constant-volume activation energy ($\Delta E^{\#}$) to the enthalpy of activation ($\Delta H^{\#}$) for the (αβ)-process plotted against density. The "isobars" are now shown with open symbols that correspond to: (squares): 0.1, (circles): 30, (up triangles): 60, (down triangles): 90, (rhombus): 120, (left triangles): 150 and (right triangles): 180 MPa.

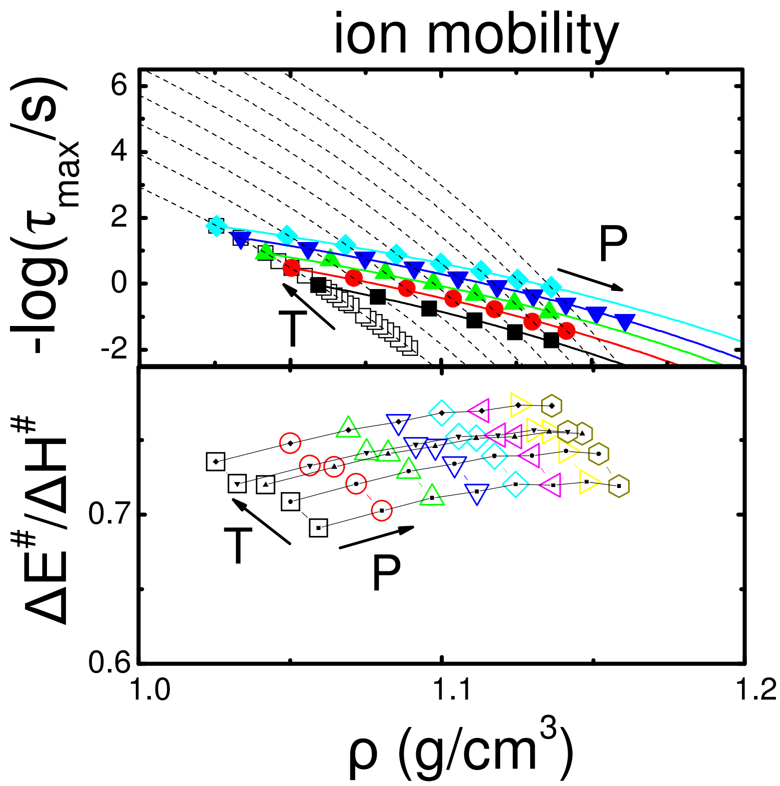

Figure S3c. (Top): Dependence of the "isothermal" (solid lines) and "isobaric" (dashed lines) relaxation times of PEMA (M_w=2.0x10^3 g/mol) on density. The "isothermal" and "isobaric" lines, are the result of the fits to the modified VFT equation (Eq. 28) to ion mobility process. The different "isotherms" are: (squares): 383.15, (circles): 393.15, (up triangles): 403.15, (down triangles): 413.15 and (rhombus): 423.15 K. In all cases the "isobaric" data at P=0.1 MPa are shown with open squares. **(Bottom)**: Ratio $\Re$, of the constant-volume activation energy ($\Delta E^{\#}$) to the enthalpy of activation ($\Delta H^{\#}$) for the ion mobility process plotted against density. The "isobars" are now shown with open symbols: (squares): 0.1, (circles): 30, (up triangles): 60, (down triangles): 90, (rhombus): 120, (left triangles): 150, (right triangles): 180 and (polygons): 210 MPa.