

# Supplementary information

## **Molecular dynamics of the asymmetric blend PVME/PS revisited by broadband dielectric and specific heat spectroscopy – Evidence of multiple glassy dynamics**

*Paulina Szymoniak, Sherif Madkour<sup>#</sup>, Andreas Schönhals<sup>\*</sup>*

Bundesanstalt für Materialforschung und –prüfung (BAM),  
Unter den Eichen 87, 12205 Berlin (Germany)

<sup>#</sup>Current address: BASF SE, Carl-Bosch-Str. 38, 67056 Ludwigshafen, Germany

HOMOPOLYMERS	$T_g^{\text{therm}}$ [K]	
PS	376	
PVME	246	
PVME/PS BLEND	$T_{g,\text{Fox}}$ [K]	$T_g$ [K]
70/30	275	256
50/50	297	273
40/60	310	279
30/70	325	-
25/75	332	293
15/85	348	352
10/90	357	363

Table S1: Composition dependence of the  $T_g$  and  $T_{g,\text{Fox}}$  of the PVME/PS blend and PVME and PS homopolymers.

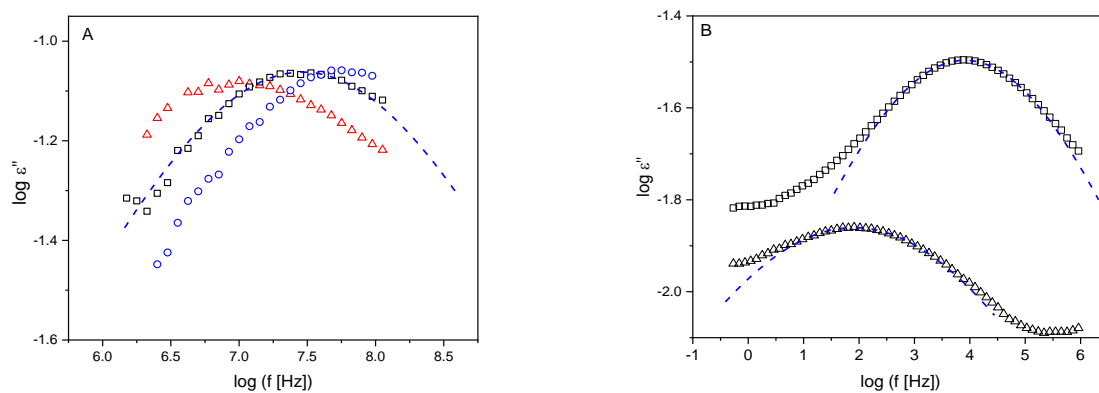


Figure S1: Dielectric loss spectra of PVME/PS 25/75 wt% versus frequency at temperatures of 349 (red triangles), 364 (black squares) and 376 K (blue circles) (frequency domain) in the high frequency range (A) and at 293 (black squares) and 243 K (black triangles) in the standard frequency range (B). The blue dashed line is an HN fit to the data.

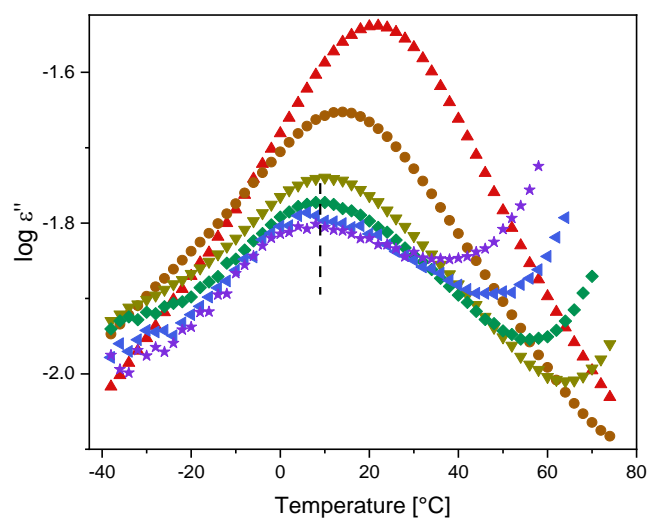


Figure S2: Dielectric loss spectra of PVME/PS 25/75 wt% versus temperature at frequencies  $\log(f \text{ [Hz]})$  of ca. 3 (red triangles), 2 (orange circles), 1 (dark-yellow down-sided triangles), 0.5 (green diamonds), 0 (blue left-sided triangles) and -0.5 (purple stars) (temperature domain).

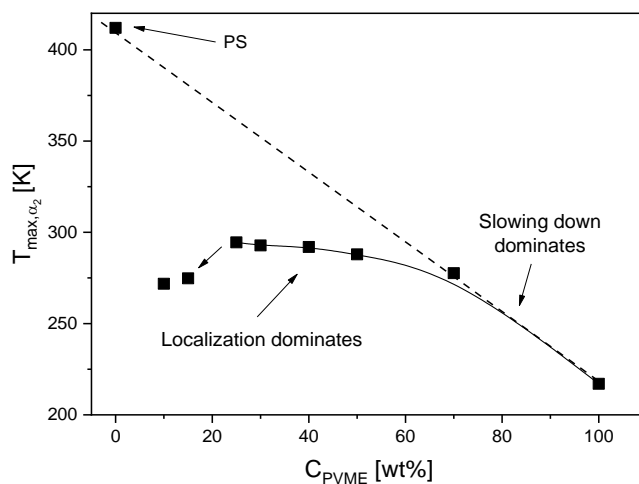


Figure S3: Peak position ( $T_{\max}$ ) of the  $\alpha_2$ -relaxation from the dielectric loss spectra obtained from the isochronal scans at 1000 Hz

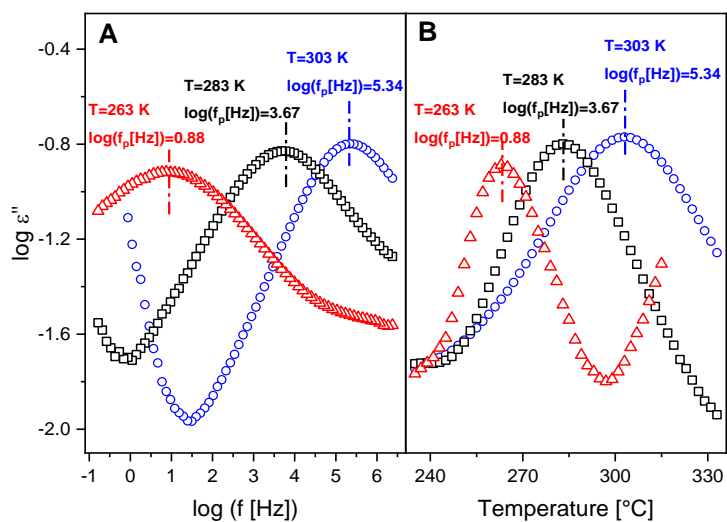


Figure S4: Dielectric loss spectra of PVME/PS 70/30 wt% as a function of (A) frequency at a temperature of 263 K, 283 K and 303 K (frequency domain) and (B) temperature at a frequency of  $\log(f_p [\text{Hz}])=0.88$ ,  $\log(f_p [\text{Hz}])=3.67$  and  $\log(f_p [\text{Hz}])=5.34$  (temperature domain).

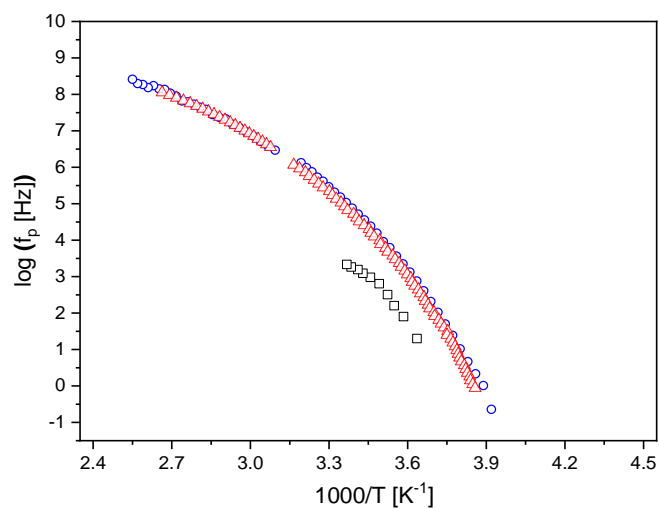


Figure S5: Relaxation map for the PVME/PS 70/30 wt% sample:  $\alpha_1$ -process (blue circles) (frequency domain),  $\alpha_2$ -process (red triangles) (temperature domain) and  $\alpha_3$ -process (black squares) (SHS).

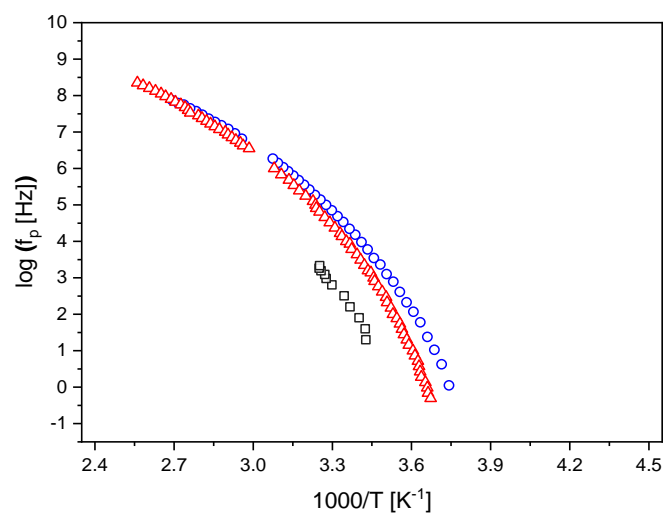


Figure S6: Relaxation map for the PVME/PS 50/50 wt% sample:  $\alpha_1$ -process (blue circles) (frequency domain),  $\alpha_2$ -process (red triangles) (temperature domain) and  $\alpha_3$ -process (black squares) (SHS).

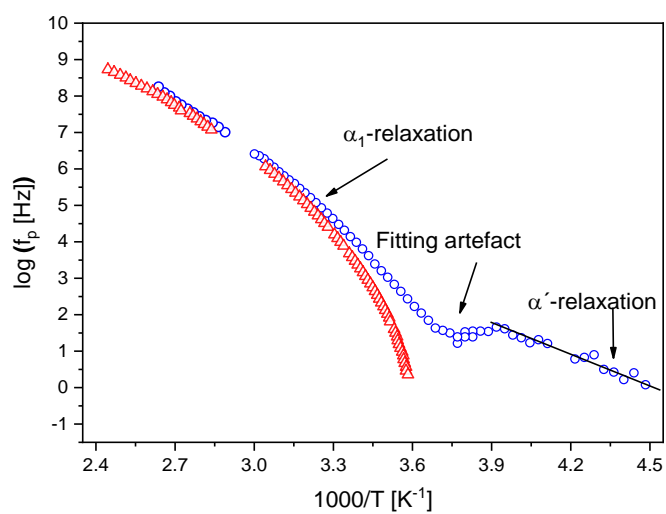


Figure S7: Relaxation map for the PVME/PS 40/60 wt% sample:  $\alpha_1$ -process (blue circles) (frequency domain) and  $\alpha_2$ -process (red triangles) (temperature domain).

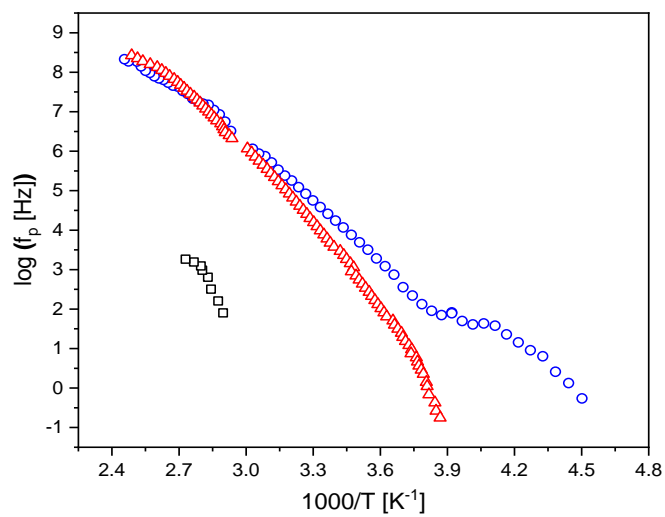


Figure S8: Relaxation map for the PVME/PS 30/70 wt% sample:  $\alpha_1$ -process (blue circles) (frequency domain),  $\alpha_2$ -process (red triangles) (temperature domain) and  $\alpha_3$ -process (black squares) (SHS).

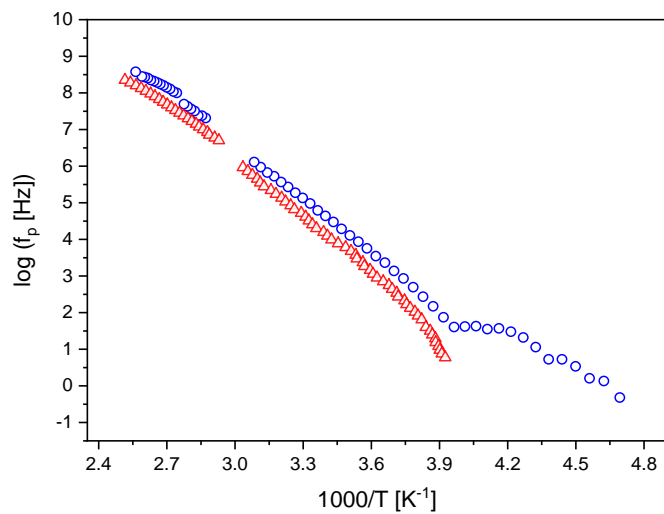


Figure S9: Relaxation map for the PVME/PS 15/85 wt% sample:  $\alpha_1$ -process (blue circles) (frequency domain) and  $\alpha_2$ -process (red triangles) (temperature domain).

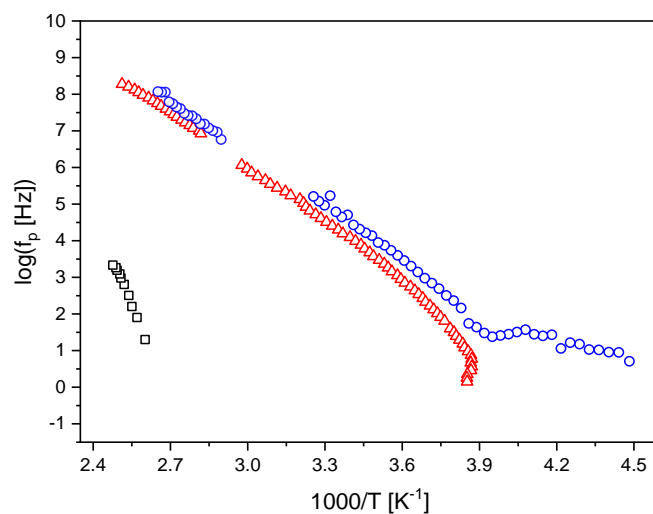


Figure S10: Relaxation map for the PVME/PS 10/90 wt% sample:  $\alpha_1$ -process (blue circles) (frequency domain),  $\alpha_2$ -process (red triangles) (temperature domain) and  $\alpha_3$ -process (black squares) (SHS).

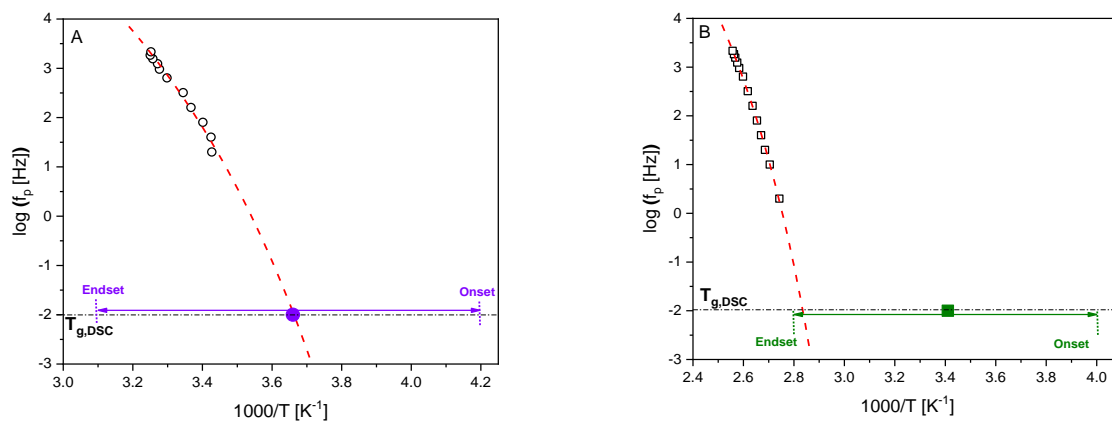


Figure S11: SHS relaxation map of (A) PVME/PS 50/50 wt% (squares) and (B) PVME/PS 25/75 wt% (circles) and glass transition temperatures obtained by DSC ( $T_{g,DSC}$ ) for (A) PVME/PS 50/50 wt% (purple circle) and (B) PVME/PS 25/75 wt% together with the onset and endset of the glass transition region. The red dashed lines are VFT fits to the data.