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Electronic Supplementary Information

Selective Molecular Annealing: *In Situ* Small Angle X-ray Scattering Study of Microwave-Assisted Annealing of Block Copolymers

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Further details on microwave heating

Microwave heating is achieved when specific atoms, molecules or ionic charged couples/adducts are exposed to an external, alternating electromagnetic field, having a frequency in the range of 0.1-300 GHz. Typically, molecular materials that are capable of interacting with microwave energy, upon exposure to its the electric field component, must be able to exhibit some form of polarisation. To achieve this they must either; (a) possess a net non-zero dipolar moment (thus exhibiting rotational polarisation), (b) be capable of becoming induced dipoles due to the localised displacement of the outer shell electron clouds with respect to the internal atomic core or (c) in the case of ionic species, they must undergo displacement polarisation i.e. an increased separation of negative and positive species occurs when in the presence of the electric field. In practice, we can measure the complex permittivity (ε^*) of a material, which determines the magnitude of the total polarisation exhibited by a material. This consists of a real part (ε') and an imaginary part (ε''), which are linked by the relationship $\varepsilon^* = \varepsilon' - j\varepsilon''$ (Equation S1). The real part is referred to as the dielectric constant and denotes the ability of the material to store electromagnetic energy within is structure and therefore determines the ability of an electromagnetic wave to propagate within the material. Whilst the imaginary part, known as the dielectric loss, indicates the ability that the material has to transfer this stored energy into heat/reactivity *via* inter-molecular motion and interaction. This interaction arises because the external electric field oscillates and so the dipolar species present in the sample try to align with the orientation of the field, so creating intermolecular motion.

Consequently, an understanding of both a material's dielectric constant and loss is essential to achieve successful simulation and understanding of the behaviour of particular system when under the influence of an electromagnetic field in the frequency range of interest.

Additionally, the propensity of a material to convert a portion of its stored energy into heat is commonly described by the dielectric loss tangent ($\tan\delta$), which is defined as the ratio of the imaginary part to the real part of the complex permittivity ($\tan\delta = \varepsilon''/\varepsilon'$ (Equation S2)). In practice, whilst the loss tangent provides limited information related to the mechanisms and interactions at molecular level, it is useful in practical situations when considering chemical/material processing. This is because it allows the microwave-absorbing characteristics of individual components to be related to the influence that they are likely to have on overall systems heating/reactivity profile.

When utilising microwave energy to selectively heat specific molecular species, it is of paramount importance to have a detailed knowledge of both the dielectric properties of the materials involved across the entire temperature range that will be involved in the process. This is because the dielectric properties vary with temperature and frequency in a non-linear fashion.[1-4] This knowledge is important because it can produce valuable information related to; (a) predicting the likely heating/reactivity profiles that the different molecular species in a mixture will achieve when exposed to microwave energy; (b) the optimisation of the design and geometry of reactors or processing apparatus used to ensure that the microwave energy penetrates the entire sample and (c) define which species are likely to undergo selective heating at a defined processing temperature. However, characterising the dielectric properties of materials to high temperatures is not a trivial task, particularly when cavity perturbation techniques are used because any distortion of the metal cavity, e.g. due to thermal expansion, can affect the resonant characteristics of the apparatus and interfere with the measurements. As a result, elaborate systems to cool the cavity are often required. Therefore, the majority of experiments for dielectric properties data acquisition tend to be conducted at, or close to, room temperature.

Dielectric Property Assessment and Estimation of Penetration Depth via Cavity Perturbation Measurements:

Material dielectric properties are highly dependent on temperature, thus those of the absorber and polymers were measured in air, over the temperature range of 20 – 180 °C with a step interval of 10 °C at 2450 MHz, to ensure that it included the full series of conditions used for the annealing of the test films (i.e. up to 150 °C for thermal annealing). These measurements were conducted using the cavity perturbation method described in previous literature reports.[1-3]. The cavity perturbation method was adopted because it is known to be better suited for measurements of low microwave absorbing materials (i.e. those with low values of ε'', also termed as low loss materials) .

The system used here was based upon a copper resonating cylindrical cavity operating at the following resonant TM_{0n0} modes; TM_{020} at 912 MHz and TM_{050} at 2450 MHz. No detailed calibration was required as the measurement is based on the differential measurement of an empty and loaded cavity relying on the monitoring of S_{21} scattering parameters. The measurement error for ε´, typically associated with this technique, is less than 2 %. Each measurement was repeated five times at the different selected bulk densities of the powdered sample or the solid cylinders (in the case of copolymers) and the mean value of measurements the associated standard deviation and the relative standard errors were determined.

The dielectric properties of the DEGDB additive and block copolymers used in this study are shown in Figure S1.

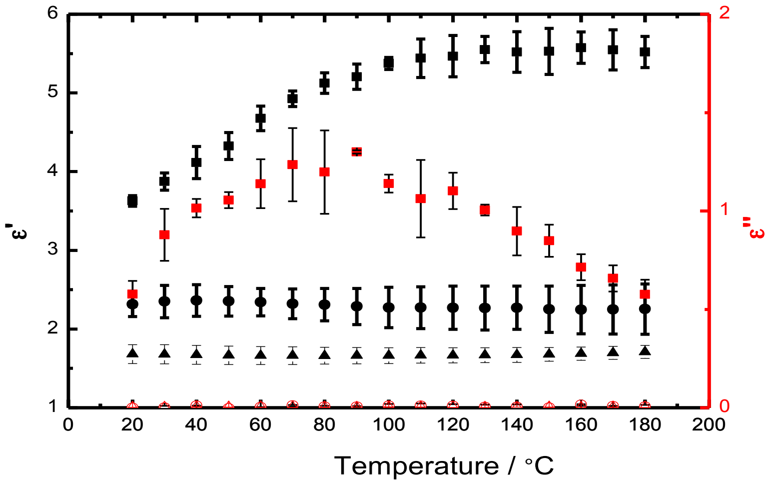

Figure S1: Plot of the variation of dielectric properties of a) Dielectric Constant (ε') (left axis, black) and Dielectric Loss (ε") (right axis, red) with temperature for DEGDB (squares), Kraton G1652 (circles) and G1657 (triangles).

The data showed that DEGDB not only had a much greater propensity to interact with the microwave energy because its ε' was double that of the polymer, but the dielectric loss values show that the polymer had essentially no ability to translate what energy that it does absorb into heat/reactivity as its ε" is essentially zero. By comparison, DEGDB exhibited good ability to translate the absorbed energy into heat/reactivity across the whole temperature range. This has been attributed to both the molecular size of the polymer and its physical form. The dipoles of solid materials and covalent bonds that are heavily constrained by being part of an extended macrostructure, such as a polymer, find it very hard to align with the phase of the microwave field. Thus, they struggle to absorb the energy and achieve the molecular motion required to translate this energy into heat *via* intermolecular friction.

To ensure that these data do not appreciably change for the polymer in the presence of a low molecular weight species, a sample of the polymer was dissolved into toluene, which is known to have a very low level of interaction with microwave energy, and the dielectric properties of this mixture were assessed and compare to that of the solvent alone (see Figure S2).

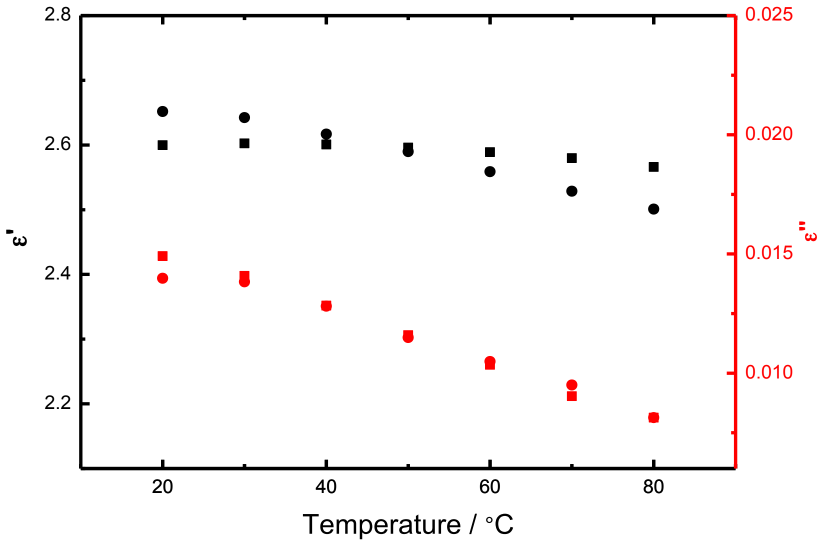

Figure S2: Plot of the variation of dielectric properties of Dielectric Constant (ε') (left axis, black) and Dielectric Loss (ε") (right axis, red) as a function of temperature for Toluene (squares) and G1652 (circles).

This data showed that the dielectric performance of the polymer : toluene mixture was essentially that of the toluene solvent alone showing that the polymer contributed negligibly to the ability of the system to heat.

Penetration Depth Estimation

For definition of the importance of the penetration depth in microweave experimentation see the main manuscript text

$$D = \frac{\lambda\sqrt{\varepsilon'}}{2\pi\varepsilon''} \qquad \text{(Equation S1)}$$

where λ is the wave length in meters of the electromagnetic wave (at the propagating frequency) and ε', ε'' are as defined in the main manuscript

Differential Scanning Calorimetry (DSC)

The thermal behaviour of the polymers was studied using differential scanning calorimetry (DSC, DSC 1 STARe, Mettler Toledo) from two heating cycles over a temperature range of -100 to 150 °C at a heating rate of 10 °C/min.

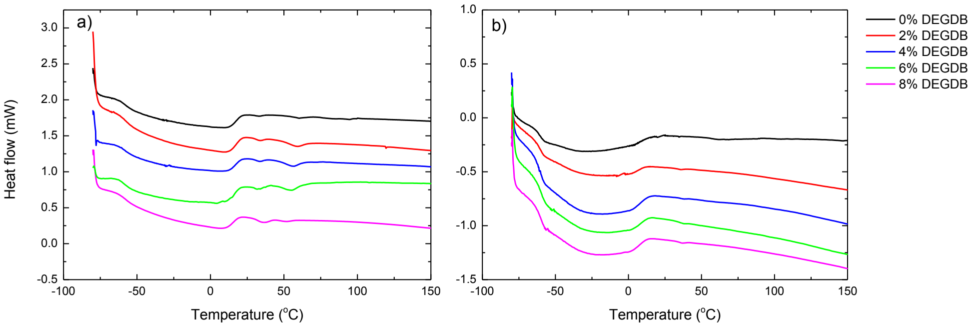

Figure S3: Differential scanning calorimetry traces for G1652 (a) and G1657 (b) with varying loadings of DEGDB; 0% (black), 2% (red), 4% (blue), 6% (green) and 8% (magenta).

Thermal and Microwave Annealing of G1657

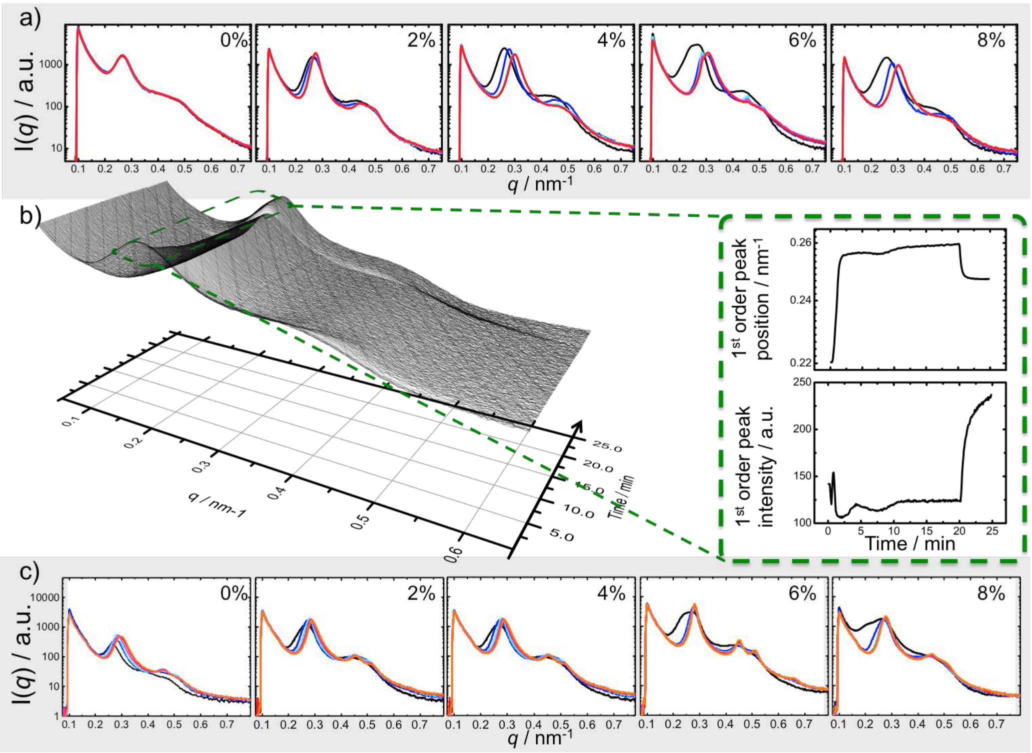

Figure S4: ***In situ*** **SAXS data during microwave annealing, where (a) shows 1D radially integrated data for G1657 SEBS with different loadings of DEGDB absorber (0%, 2%, 4%, 6% and 8%) at different microwave exposure times: 0 (black), 1.5 (blue), 7.25 (cyan), 13 (magenta) and 18.75 (red) minutes; (b left) time-resolved 1D radially integrated data for G1657 SEBS with 8% DEGDB absorber, (b right) peak position (top) and peak (bottom) as a function of time for G1657 SEBS with 8% DEGDB absorber; (c) shows 1D radially integrated data for G1657 SEBS with different loadings of DEGDB absorber (0%, 2%, 4%, 6% and 8%) thermally annealed at 150 °C for: 0 (black), 1.5 (blue), 7.25 (cyan), 13 (magenta), 18.75 (red) and 24.5 (orange) minutes.**

Thermal annealing of a bilayer film comprising G1652 (layer 1) with G1657 + 6% DEGDB (layer 2).

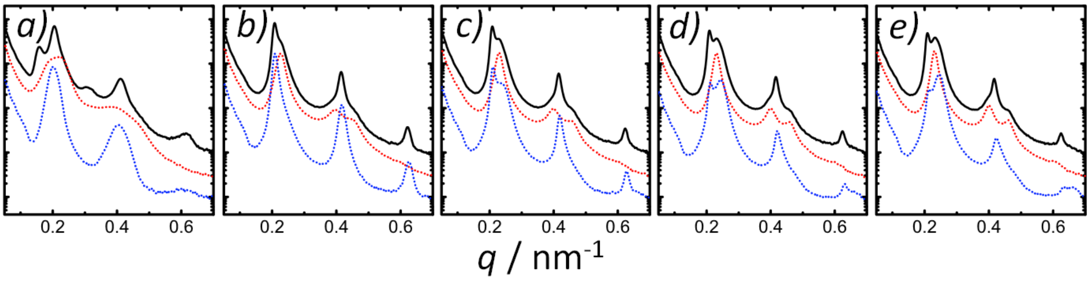

Figure S5: **1D radially integrated SAXS data for the thermal annealing of a bilayer film (black) comprising G1652 (layer 1) with G1657 + 6% DEGDB (layer 2), with comparative single layers films G1657 +6% DEGDB (green) and un-doped G1652 (purple), with curves offset along the logarithmic intensity axis for clarity for: 0 (a), 1.5 (b), 7.25 (c), 13 (d) and 18.75 (e) and 24.5 minutes.**

Materials

G1652 and G1657 was kindly supplied by Kraton Polymers Belgium and was used as received. Kraton G1652 is a SEBS copolymer containing 30 wt% PS, with a number-average molecular weight (M_n) of 55.8 kg mol^{-1}, polydispersity index of (M_n/M_w) of 1.01.Kraton G1657 is a blend of SEB and SEBS copolymers, containing 13 wt% PS, with two distinct molecular weight species at 55.6 and 109 kg mol^{-1}, with polydispersity indices of 1.02 and 1.08, respectively. GPC traces are shown in Figure S5.

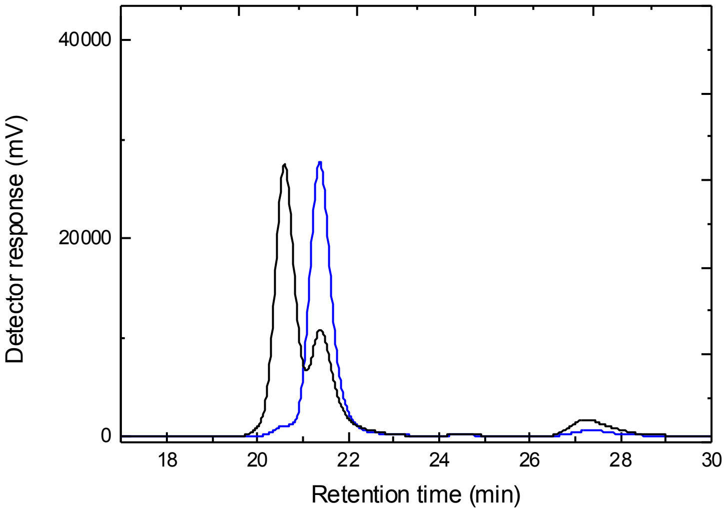

Figure S5: GPC traces of Kraton G1652 (blue line) and Kraton G1657 (black line).

Supplementary Table S1: Molar mass data for Kraton G1652 and Kraton G1657 derived from GPC.

	M_n (kg mol^{-1})	M_w / M_n
G1652	55.8	1.01
G1657*	82.5	1.08

N.B. G1657 is a blend of two BCPs, SEB and SEBS, with M_p ~ 55.6 and 109 kg mol^{-1}, respectively.

Diethyleneglycoldibenzoate (DEGDB, 90%, Sigma Aldrich) and Tetrahydrofuran (THF, Laboratory Grade, Fisher) were used as received.

References

1. Smith, A. D.; Lester, E. H.; Thurecht, K. J.; Kingman, S. W.; Harfi, J. E.; Dimitrakis, G.; Robinson, J. P.; Irvine, D. J. Temperature dependence of the dielectric properties of 2,2′-azobis(2- methylbutyronitrile) (AMBN). Ind. Eng. Chem. Res. 2010, 49, 3011.
2. Meredith, R. J. Eng. Handbook Ind. Microwave Heating. IEEE: London, 1998.
3. Lester, E.; Kingman, S.; Dodds, C.; Patrick, J. The potential for rapid coke making using microwave energy. Fuel 2006, 85, 2057.
4. Metaxas A.C., Meredith R.J., Industrial Microwave heating; Peter Peregrinus Ltd. 1983