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Supporting information for

Shape-Memory Effect in Ionic Elastomers: Fixation through Ionic Interactions

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Shape-memory effect on ionic elastomers

The video file entitled "SupportingInformation_SMEInIonicElastomers_Video.mov" contains a movie that demonstrates a shape-memory cycle wherein rubber sample M4D05 shows its elastomeric behaviour at room temperature, being then heated and programmed for shape fixing at 150 °C. The helicoid (temporary) shape is fixed by cooling down the sample at 25 °C. It is important to note that the use of the so-named ionic transition as the unique switching mechanism for the activation of the SME does not modify the elastomeric behaviour of this material. Finally, the sample is heated up to 150 °C and complete the shape recovery over the course of several seconds is observed. It is important to point out that in both permanent and temporary shape the soft matrix maintains its elastic behaviour.

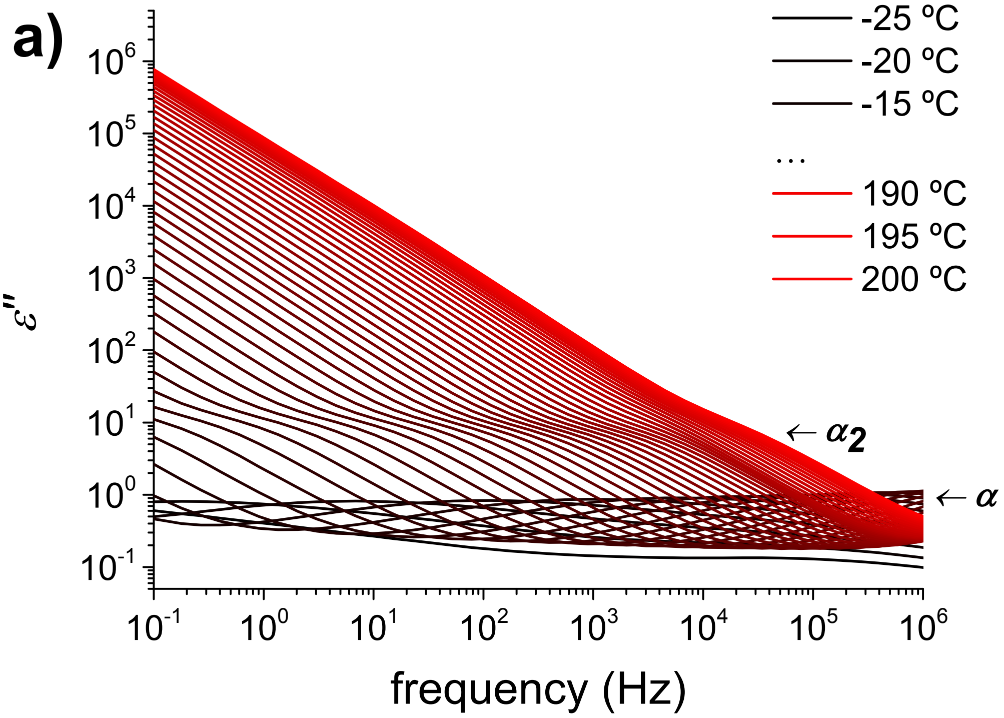
Broadband dielectric spectroscopy (BDS)

BDS measurements were performed on an ALPHA high resolution dielectric analyzer (Novocontrol Technologies GmbH). The samples were mounted in the dielectric cell between two parallel gold-plated electrodes. The complex permittivity ε^* of each sample was calculated from the measurement of the complex impedance. [[1] D. Boese and F. Kremer, *Macromolecules*, 1990, **23**, 829–835.] The complex permittivity was measured over a frequency window of $10^{-1} < F/\mathrm{Hz} < 10^{7}$ ($F = \omega/2\pi$ is the frequency of the applied electric field being ω the angular frequency) in the temperature range from −100 °C to 200 °C in 5 °C steps, where ε' and ε'' are the real and imaginary parts of the complex permittivity.

Ionic sample show three processes in the BDS measurements as it is shown in **Figure S1**, the α process corresponding to segmental motions at high ω, the α_2 process corresponding to ionic dissociation at medium ω and the electrode polarization at low ω. The dielectric relaxation of the XNBR ionomer shows a strong electrode polarization process that masks the α_2 relaxation in the dielectric loss ε'' (see **Figure S1a**). Consequently, the derivative formalism $\varepsilon_{\mathrm{der}} = (-\pi/2)\, \mathrm{d}\varepsilon'/\mathrm{d} \ln \omega$ is required in order to eliminate the Ohmic conduction and elucidate low ω processes [[2] M. Wübbenhorst and J. van Turnhout, *J. Non. Cryst. Solids*, 2002, **305**, 40–49.]. This formalism is based on the interrelation between ε' and ε'' by the Kramers-Kronig transform, which can be performed according to the logarithmic derivative showed in [[2] M. Wübbenhorst and J. van Turnhout, *J. Non. Cryst. Solids*, 2002, **305**, 40–49.] where $\varepsilon_{\mathrm{der}}$ approximately equals the Ohmic-conduction-free dielectric loss ($\varepsilon''_{\mathrm{rel}}$) for rather broad peaks (e.g. the α_2 relaxation in ionomers). **Figure S1b** shows two clearly separated relaxations (identified as α and α_2 processes) which were analyzed by the phenomenological Havriliak–Negami (HN) function [[3,4] S. Havriliak and S. Negami, *Polymer*, 1967, **8**, 161–210.; F. Kremer and A. Schönhals, in *Broadband Dielectric Spectroscopy*, Springer, Berlin, Heidelberg, 2003, pp. 99–129.]

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

where $\Delta\varepsilon$ is the relaxation strength ($\Delta\varepsilon = \varepsilon_s - \varepsilon_\infty$, ε_∞ and ε_s are the unrelaxed and relaxed values of the dielectric constant), τ_{HN} is the characteristic relaxation time, and b and c are shape parameters ($0 < b$, $c \leq 1$) which describe the symmetric and the asymmetric broadening of the equivalent relaxation time distribution function, respectively.



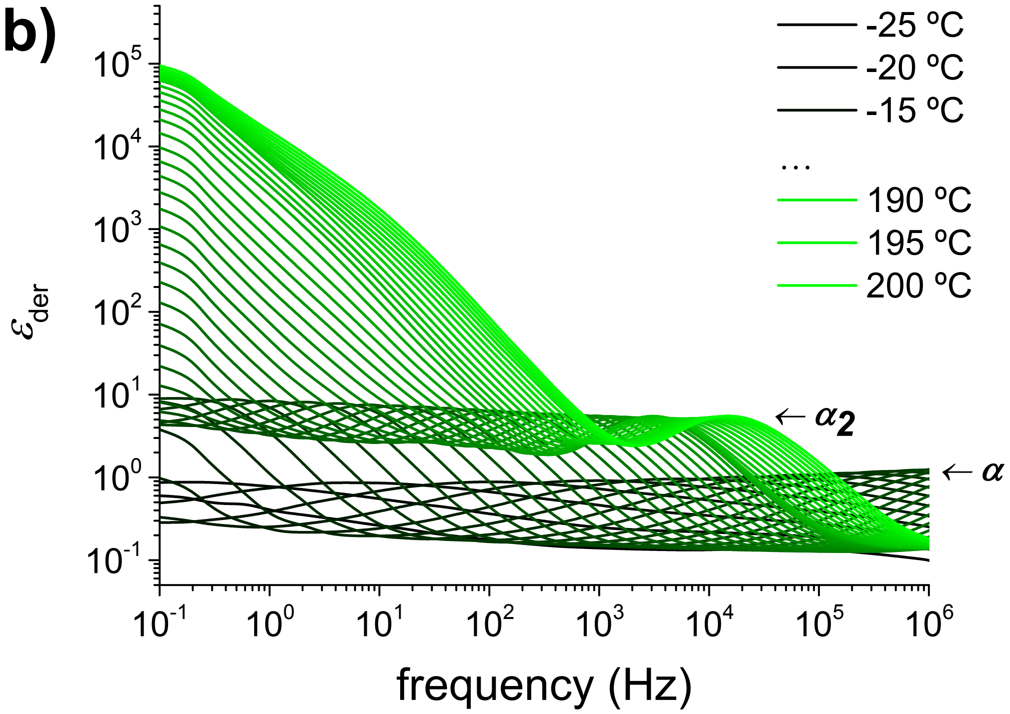


Figure S1. (a) Dielectric loss and (b) derivative formalism of dielectric spectra, $\varepsilon_{der} = (-\pi/2)\ d\varepsilon'/d\ \ln\omega$, plotted against the frequency F for the M4D0 sample (XNBR-MgO ionomer) from -25 to 200ºC in steps of 5 ºC.

Accordingly, the frequency of dielectric maximal loss ω_{max} ($\varepsilon_{der} \approx \varepsilon''_{rel}$) obtained for the α_2 process from this analysis (see **Figure S1b**) is plotted against 1000/T in **Figure 3** in the main text. The curve in **Figure 3** is the Vogel-Fulcher-Tammann (VFT) fittings: $\omega_{max} = \omega_0 \exp[-DT_0/(T - T_0)]$, where ω_0 is the attempt frequency, T_0 is the Vogel temperature and D is the so-called strength parameter. According to the best obtained fitting, the low D value ($D = 4.2 \pm 0.3$) demonstrates the fragility (large deviation from an Arrhenius-like behavior) of the ionic association/dissociation process in the studied XNBR-Mg ionomer. Additionally, the Vogel temperature was kept as a free fitting parameter in the data analysis, obtaining a value around 228 K, which corresponds to $T_0 \approx T_g - 25$ K.

The ionic dissociation/association process activates a dielectric α_2 relaxation that corresponds to a characteristic viscoelastic modulus of kT per ionic group: $G'(\omega_c) = P_0kT$, being P_0 the number density of ionic groups, k the Boltzmann constant and T the temperature, respectively. According to the storage modulus, G', corresponding to the frequency of dielectric maximal loss (ω_{max}) obtained from rheometric measurements (see **Figure S2**), the number density of ionic groups for XNBR-Mg should be around 0.8 nm^{-3} that is in a reasonable agreement with the value of P_0 = 0.9 nm^{-3} obtained from the information supplied by the rubber manufacturer.

Additionally, from the characteristic time given in the dielectric process, the slow viscoelastic relaxation process showed in **Figure S2** could be predicted using a sticky-Rouse model [[5] Q. Chen, G. J. Tudryn and R. H. Colby, *J. Rheol.*, 2013, **57**, 1441–1462.]. However, the presence of entanglement constraints in the XNBR sample can complicate the mechanism since the stress relaxation has contributions from both dissociation of stickers (ionic associations) and chain reptation [[6] L. Leibler, M. Rubinstein and R. H. Colby, *Macromolecules*, 1991, **24**, 4701–4707.]

Flow properties

Rheometric Measurements were performed in a rubber process analyzer RPA 2000 to study the flow properties of XNBR samples vulcanized with different vulcanization systems. Three covalent networks, named M0D05, M0D1 and M0D2, were prepared by adding different concentrations of dicumyl peroxide (0.5, 1 and 2 phr). The ionic sample contained 4 phr of MgO (sample M4D0) whereas the mixed samples (named M4D025, M4D05 and M4D1) were compounded with 4 phr of MgO and varying the peroxide content (0.25, 0.5 and 1 phr).

The Frequency-sweep experiments were carried out after the vulcanization process. The shear modulus was measured at frequencies from 0.002 to 33.33 Hz at temperatures from 40 to 230 °C. Using the frequency−temperature superposition [[7] J. D. Ferry, *Viscoelastic Properties of Polymers*, John Wiley & Sons, Third Edit., 1980.], a combined master curve was plotted to obtain the stress relaxation of the shear modulus (*G'*) in a wide range of frequencies (see **Figure S2**).

Ionic interactions are dynamic bonds that can selectively undergo reversible rearranges between aggregates after a certain characteristic lifetime (see **Figure 3** in the main text). Consequently, their efficiency as active cross-link points strongly depends on the studied time-scale. **Figure S2** shows the effect of ionic rearrangement lifetimes on the terminal chain dynamics for different XNBR samples. Polymer chains in XNBR ionomers can flow via ionic exchanged between discrete aggregates without breaking all their ionic associations simultaneously, but this slow process requires high temperatures to take place on manageable time for activate/deactivate in an effective way the shape memory properties of these materials. Opposite to this behavior, XNBR matrix covalently cross-linked by using 2 phr of dicumyl peroxide (M0D2 in **Figure S2**) reveals a clear elastic plateau over a wide range of temperatures and frequencies. At lower concentrations of DCP, the plateau is obtained at lower *G'* values because of the decreasing of cross-link density until at 0.5 phr of DCP (or lower concentration of peroxide, data does not shown) it is not possible to observe a constant *G'* value at high temperatures. This behaviour could be related to formation of cross-links between rubber chains but they are not enough to create a covalent network that avoids the polymer flow [see [8] I. Mora-Barrantes, M. A. a. Malmierca, J. L. Valentin, a. Rodriguez and L. Ibarra, *Soft Matter*, 2012, **8**, 5201. for additional information about this issue].

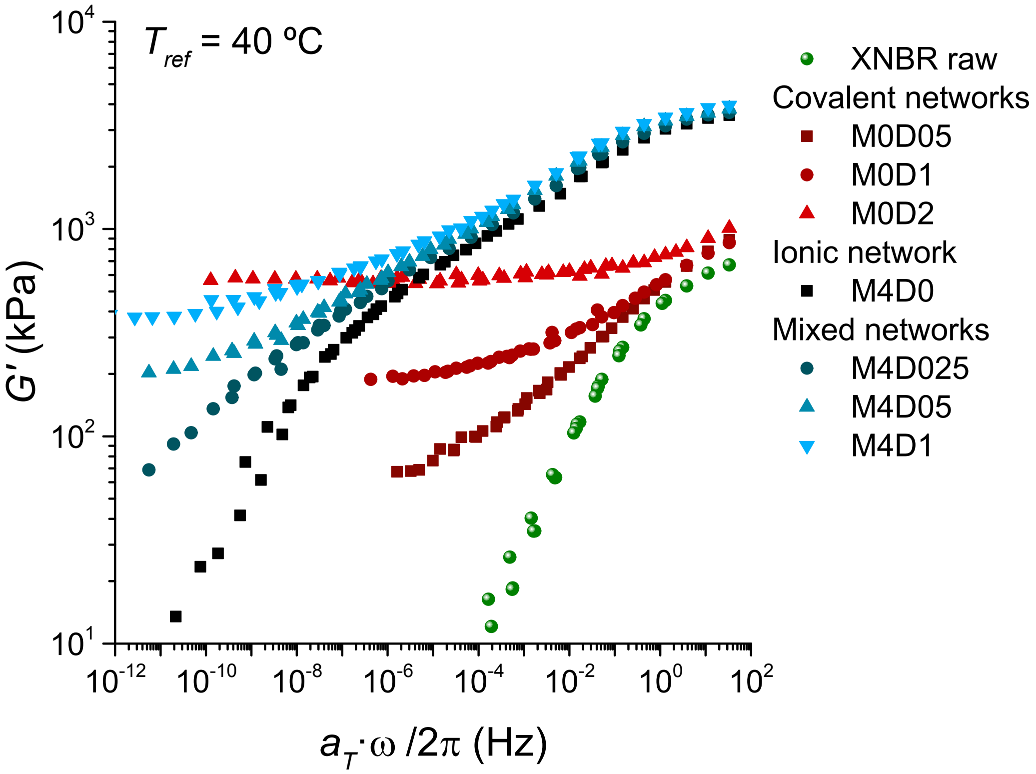


Figure S2. Master curves of storage modulus, *G'*(ω), as function of angular frequency ω for ionic, covalent and mixed XNBR samples obtained by measuring the shear modulus at different frequencies and temperatures, plotted for a reference temperature of 40 °C. The displacement factors used for frequency−temperature superposition were different for each sample.

Addition of increasing amounts of DCP to the ionic elastomer (maintaining constant the concentration of MgO) reduces the chain mobility of XNBR ionomers and consequently the polymer flow dynamics shift to larger time-scales. The polymer flow of XNBR ionomers is completely suppressed only when a covalent network is formed (at DCP concentrations higher than 0.5 DCP).

Tensile properties

Tensile tests were performed in an Instron model 3366 dynamometer equipped with a video camera to measure deformations at a strain rate of 500 mm·min^{-1} on Type-II dogbone-shaped samples with 2 mm of thickness, according to the standard ISO 37. Five specimens for sample M4D05 were tested at 25 ± 1 ºC and the results are reported in **Figure S3**. The tensile curves show the typical shape for elastomers, but M4D05 sample reach tensile strength values higher than 40 MPa with elongation at break larger than450%. Those tensile properties are considerably enhanced with respect any (unfilled) rubber matrix vulcanized with covalent systems because of the effect of the trapped rubbed fraction around ionic interactions that act as reinforcing points [8,9 I. Mora-Barrantes, M. A. a. Malmierca, J. L. Valentin, a. Rodriguez and L. Ibarra, *Soft Matter*, 2012, **8**, 5201.; M. A. Malmierca, A. González-Jiménez, I. Mora-Barrantes, P. Posadas, A. Rodríguez, L. Ibarra, A. Nogales, K. Saalwächter and J. L. Valentín, *Macromolecules*, 2014, **47**, 5655–5667.].

The inset graph shows the stress at low deformations, where the three different programming strains applied in the shape memory test have been marked. It is important to note the lower stress required to achieve a given strain in the shape-memory cycles compared to the tensile properties measured in the dynamometer. These divergences are caused by the deformation rate. At a strain rate of 500 mm·min^{-1} dynamical effects should be taken into consideration, whereas the quasi-static conditions applied in the shape-memory cycles minimize these dynamical contributions.

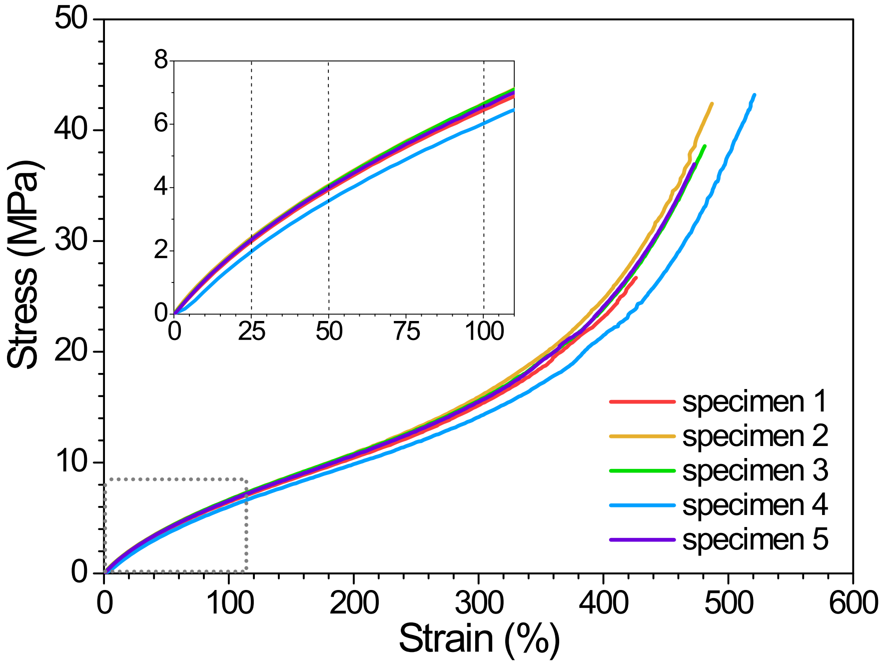


Figure S3. Tensile tests of sample M4D05 for 5 specimens. The inset graph is a magnification of the first part of the test.

Formation of covalent cross-links on XNBR rubber at high temperature

The elastic torque (*S*') was measured as a function of time to evaluate the formation of cross-links at 160 and 200 ºC in raw XNBR samples without any vulcanization system (**Figure S4**). Rheometry curves were obtained in a Rubber Process Analyzer RPA 2000 (Alpha Technologies) with a deformation of 6.98 % and an oscillatory frequency of 1.667 Hz (the same conditions usually applied to obtain the vulcanization curves in elastomers). The significant increase of *S*' demonstrates the continuous auto-formation of additional cross-links in XNBR samples at temperatures above 200 ºC. In absence of any additional chemical in the system, the origin of this reaction should be derived from the chain scission reactions that should be the source of radicals that promotes the cross-linking reaction. In this way the polybutadiene rubber (BR) and its derivate rubber matrices, e.g. XNBR, are characterized by a high efficiency in the vulcanization via radical pathways because the cross-linking reactions are favoured against other side reactions [[10] J. L. Valentin, P. Posadas, A. Fernandez-Torres, M. A. Malmierca, L. Gonzalez, W. Chasse and K. Saalwächter, *Macromolecules*, 2010, **43**, 4210–4222.].

This is an important fact to take into consideration because temperatures around 200 ºC should be considered as the upper temperature limit in the design of shape memory cycles for XNBR and all the other rubber matrices that contains butadiene monomers in the backbone structure.

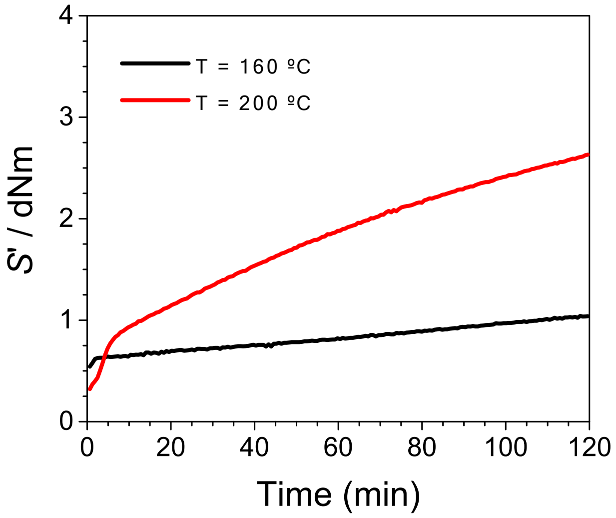


Figure S4. Vulcanization curves of raw XNBR without any cross-linker at 160 and 200 ºC, respectively.