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Viscoelasticity of main chain liquid crystalline elastomers

Marta Giamberini [a,*], Veronica Ambrogi [b], Pierfrancesco Cerruti [b,c], Cosimo Carfagna [b,c]

[a] Istituto per i Materiali Compositi e Biomedici, Consiglio Nazionale delle Ricerche, Piazzale Tecchio 80, 80125 Napoli, Italy
[b] Dipartimento di Ingegneria dei Materiali e della Produzione, Università di Napoli 'Federico II', Piazzale Tecchio 80, 80125 Napoli, Italy
[c] Istituto di Chimica e Tecnologia dei Polimeri, ICTP-CNR, Via Campi Flegrei 34, 80078 Pozzuoli, Naples, Italy

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Abstract

Time–temperature superposition (TTS) principle was applied to dynamic mechanical analysis performed on two main-chain polydomain elastomers exhibiting a nematic and a smectic A phase. It was found that TTS did not hold neither across the nematic–isotropic nor the smectic–isotropic transitions. The nematic elastomer showed an increase in the storage modulus in the isotropic phase with respect to the nematic phase: this could be explained by means of dynamic soft elasticity, which has been claimed in some literature for side-chain liquid crystalline elastomers (SCLCEs), or in terms of the de Gennes model by a macroscopic/hydrodynamic description. The presence of the mesogen directly incorporated into the main chain increases the lifetimes of the elastic modes both in the isotropic and in the liquid crystalline (LC) phases, with respect to the SCLCEs. In the case of the smectic A elastomer, lifetimes on the order of 10^9 s could be estimated.

Keywords: Liquid crystalline elastomers (LCE); Viscoelasticity; Time–temperature superposition

1. Introduction

Liquid crystalline elastomers have been the object of growing interest in recent years, due to their peculiar features, which arise from the combination of elastic properties of conventional elastomers and orientational properties of liquid crystals [1,2]. Interest in such materials grows from their potential applications in the field of mechanical actuators (artificial muscles), optics and coatings of materials, which can efficiently dissipate mechanical energy for, e.g. automotive and aerospace industry. Many papers recently appeared, which deal with mechanical, dynamic-mechanical and rheological properties of side-chain liquid crystalline elastomers (SCLCEs) both on polydomain samples (in which the mesogenic groups are macroscopically disordered) and on monodomain samples (in which the mesogenic groups are macroscopically ordered) [3–18]. On the contrary, few papers examined the mechanical and dynamic-mechanical properties of main-chain liquid crystalline elastomers [19–22] or SCLCEs containing a main-chain LC polymer [11]. To our knowledge, in the literature no papers exist which deal with the viscoelastic properties of main-chain LCEs. In recent papers, we reported the synthesis, physico-chemical and mechanical properties of main-chain LCEs obtained by reacting mesogenic epoxy terminated molecules with dicarboxylic aliphatic acids of different length [23,24]. In this paper, we performed dynamic mechanical thermal analysis (DMTA) frequency sweep analyses in the shear sandwich configuration on two main-chain polydomain elastomers, namely PHBHQ–AA and PHBHQ–SA, which exhibit nematic and smectic A phase, respectively. We subsequently applied the time–temperature superposition (TTS) principle to DMTA data and compared our results with the ones reported for SCLCEs in the literature.

2. Experimental part

4′-(2,3-Epoxypropoxy)phenyl-4-(2,3-epoxypropoxy)benzoate (PHBHQ) was synthesized as previously reported [23]. Adipic acid (AA) and decanedioic acid (SA) were purchased from Aldrich Chemical Co. and used without any further purification. The LCE PHBHQ–AA and PHBHQ–SA were prepared as described in Ref. [23]. Molecular formulas of the LCE under investigation are reported in Scheme 1.

The range of linear viscoelasticity of all the samples was checked by means of a strain controlled rotational rheometer (mod. ARES L.S., Rheometric Scientific). Dynamic strain sweep tests were carried out by using parallel plates (diameter 8 mm) in inert atmosphere with a gap between the plates of

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* Corresponding author. Tel.: +34 09775558286.
E-mail address: marta.giambeini@urv.net (M. Giamberini).

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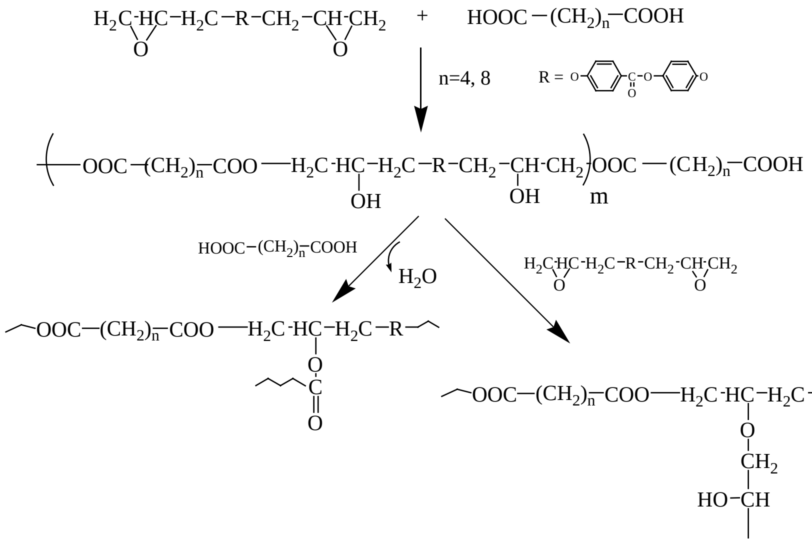

Scheme 1.

about 1 mm. The temperatures selected were: $T=50\ ^\circ\mathrm{C}$ for both elastomers in the LC phase, and $T=75$ and $100\ ^\circ\mathrm{C}$ for isotropic PHBHQ–AA and PHBHQ–SA, respectively. The range of investigated deformation was 0.01–5%. For all the samples three frequencies were selected, 0.1, 1 and 10 Hz.

DMTA experiments were performed on polydomain samples by means of TA Instrument 2980 dynamic mechanical analyzer in the shear sandwich configuration in the variable frequency mode. Surface areas of the samples were about 80 mm^2 and their thickness was typically 1 mm but slightly varied from sample to sample and was measured by a micrometer individually for each sample. The amplitude of the applied deformation was 8 μm, making the sample shear strain approximately 0.8%, which is within the linear viscoelasticity range of the systems. The experiments were performed in the following way: samples had been previously annealed in the isotropic phase (at 90 °C in the case of PHBHQ–AA and 120 °C in the case of PHBHQ–SA) for 30 min, then frequency sweep was performed between 200 and 0.01 Hz, samples were subsequently cooled down 5 °C and equilibrated at this temperature for 30 min; frequency was swept again between 200 and 0.01 Hz. The whole process was repeated down to a final temperature of 30 °C. In the isotropic phase, the time set for the sample to equilibrate is longer than the longest relaxation time, as experiments will show later. In the LC phase, much longer relaxation times result; however, we expect that the results reported for the LC phases are at least qualitatively correct. Master curves were built by means of TA Rheology Advantage Data Analysis V5.0.38.

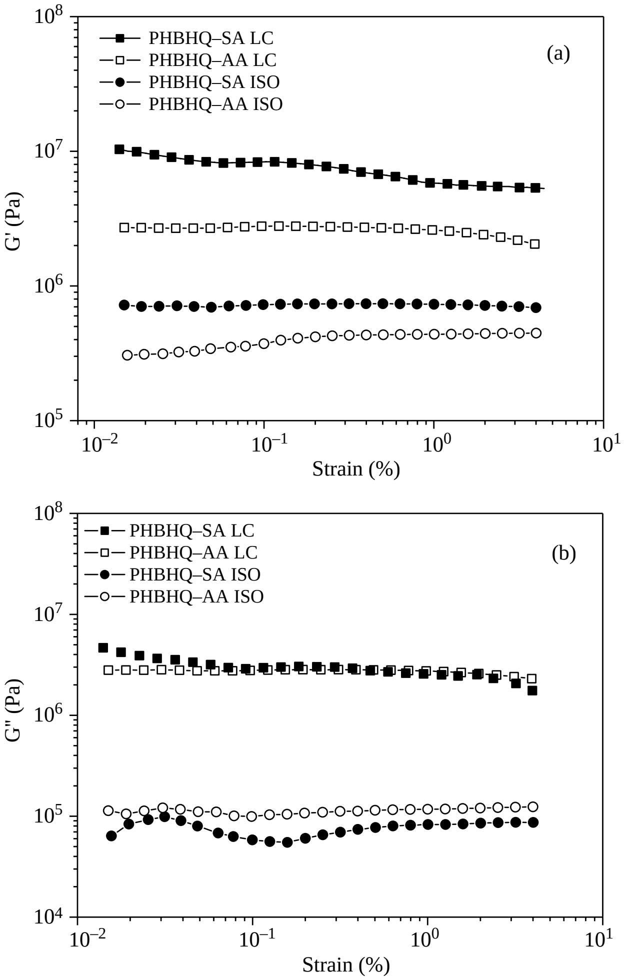

Fig. 1. Variation of the viscoelastic properties versus strain amplitude for LC and isotropic PHBHQ–AA PHBHQ–SA elastomers. (a) Storage modulus G'; (b) loss modulus G''.

3. Results and discussion

3.1. Rheological measurements

Fig. 1(a) and (b) displays the variation of the storage modulus G' and loss modulus G'', respectively, versus strain amplitude for the two elastomers, in both LC and isotropic phase at 1 Hz. The storage modulus, within the limits of experimental errors, is not strain dependent in the whole strain region up to 5%. The general behaviour of the loss moduli with strain is similar to that described for the storage moduli.

Due to the higher testing temperatures of isotropic samples, the latter exhibit lower shear moduli.

The experiments carried out at different frequencies (0.1 and 10 Hz) are not shown, as they exhibited a behaviour comparable with that observed at 1 Hz. The above reported results, suggested that our samples are in their linear response regime at strain values well above 0.8%, which is the shear strain value used for DMTA experiments described afterwards.

3.2. DMTA characterization

3.2.1. PHBHQ–AA system

This systems exhibits a T_g of 37 °C and a nematic phase up to 61 °C, as it was previously reported [23]. Fig. 2 reports the master curves for the phase shift ϕ for sample PHBHQ–AA, obtained from the superposition of measurements taken at 30, 35, 40, 45, 50, 55 and 60 °C (nematic phase) and 65, 70, 75, 80 and 85 °C (isotropic phase). 65 °C was chosen as the reference temperature.

The time–temperature superposition (TTS) principle cannot be applied through the N-I transition for this system and a continuous behaviour is shown only in the temperature range corresponding to the isotropic phase. Therefore, the two data sets (30–60 and 65–85 °C) have been treated separately and we built master curves for the isotropic and the nematic phase, respectively. It was already reported that time–temperature superposition does not work across the nematic–isotropic transition for main chain polymers [25,26]. From Fig. 2 it is also evident that the isotropic elastomer is in its hydrodynamic regime for $\nu \leq 10^{-2}$ Hz, when $\phi \approx 0$, and this is in agreement with DMTA experiments in the fixed frequency mode previously reported [24], where resulted that the truly elastic regime could be reached at 0.01 Hz at about $T_i + 25$ °C. The phase shift increases strongly with frequency and reaches a maximum value of about 36° at about 10 Hz; for higher frequencies, it decreases rapidly. Frequency values higher than 10^3 Hz could not be investigated because this would imply measurements at lower temperatures, when the TTS principle fails due to the transition to the nematic phase.

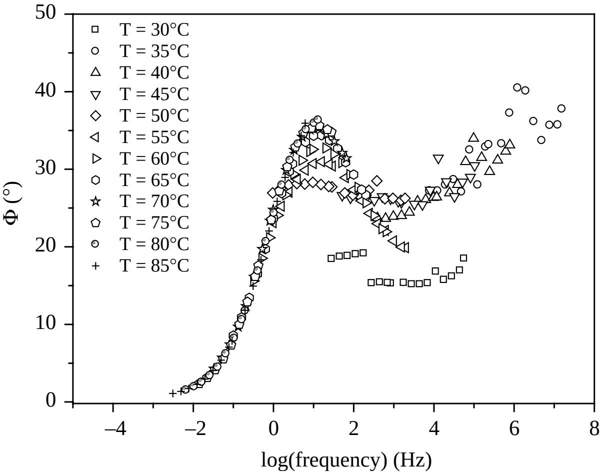

Fig. 2. Master curve for the phase shift ϕ for sample PHBHQ–AA, obtained from the superposition of measurements taken between 30 and 85 °C. Reference temperature: 65 °C.

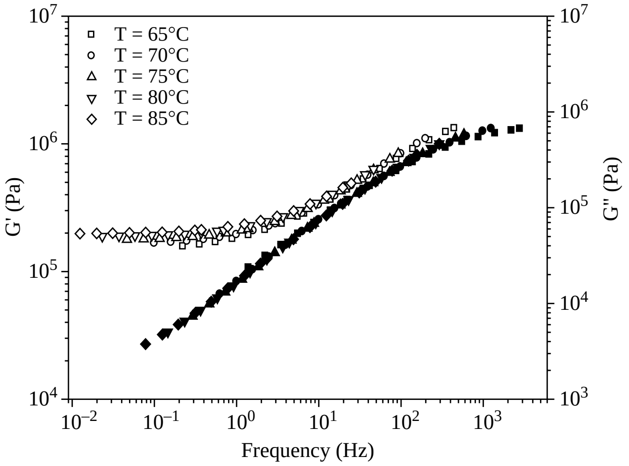

Fig. 3. Master curves of G' (open symbols) and G'' (black symbols) in the isotropic phase of PHBHQ–AA. Reference temperature: 70 °C.

Fig. 3 reports the master curves of G' and G'' in the isotropic phase of PHBHQ–AA, obtained from the superposition of measurements taken at 85, 80, 75, 70 and 65 °C; 70 °C was chosen as a reference temperature. At low frequencies, G' shows a plateau characterizing the permanent network and G'' rapidly decreases. For frequencies ν comprised between 1 and 10^3 Hz, G' and G'' increase with a power law $G'(\nu) = G''(\nu) \sim \nu^{\xi}$ with $\xi = 0.37 \pm 0.01$. In the isotropic phase of side-chain liquid crystalline elastomers (SCLCEs) a power law ν^{ξ} with $\xi = 0.5$ has been frequently found [5,8,12]. The origin of this scaling behaviour was ascribed to the presence of transient clusters of macroscopic size ($\sim$10–50 μm) [5]; however, it was also shown that the value of the exponent is not universal: in the case of experiments performed on side-chain liquid crystalline polymers (SCLCPs), a scaling law with an exponent of 0.6–0.7 resulted [27]. The numerical difference in the values of the exponent of SCLCPs and SCLCEs was ascribed to the influence of the permanent network on the spectrum of relaxation times of the transient clusters. Therefore, it seems reasonable to conclude that the dependence of the response on frequency depends on the material composition and that great differences can be expected when the mesogenic moieties are incorporated into the main chain as in our case.

The purely elastic response could only be observed in the isotropic phase at high temperatures and very low frequencies. As the response of the system is no longer hydrodynamic above 10^{-2} Hz, (Fig. 2) we can deduce that the relaxation time of the longest lived mode in the isotropic phase is on the order of 100 s: in the case of side-chain LC elastomers in the isotropic phase smaller values (10^{-2}, 10^{-1} s) were found [5,8,12].

In Fig. 4, the temperature dependence of the shift factors a_T used for superposition of curves in the isotropic phase is plotted. The shift factors can be fitted rather well to the

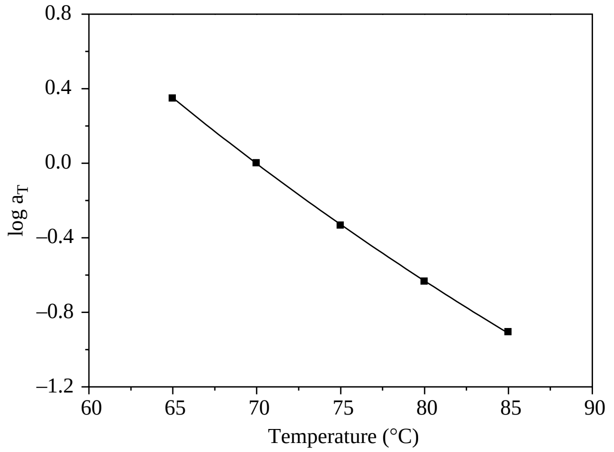

Fig. 4. Temperature dependence of the shift factors a_T used for superposition of curves of PHBHQ–AA in the isotropic phase and corresponding fit with the WLF law.

empirical Williams–Landel–Ferry (WLF) relationship [28]

$$\log a_T = -C_1 \frac{T - T_{\text{ref}}}{T - T_{\text{ref}} + C_2}$$

with $C_1 = 8.6$ and $C_2 = 126.2$.

Figs. 5 and 6 report, on the left axis, the master curves of G' and G'', respectively, for PHBHQ–AA in the nematic phase at 30, 35, 40, 45, 50 °C. The reference temperature was 50 °C. As a first remark, it must be underlined that we could not find a unique set of time–temperature shift factors to superpose the storage and loss moduli simultaneously (the shift factors for G' and G'' only have the same value at 45 °C). When we attempted to build the Master Curve for G', then the corresponding shift factors applied to G'' data produced a quite poor result (right axis of Fig. 5). Analogously, when we attempted to superpose the G'' data, we got a quite reasonable result, but these shift factors applied to G' data clearly gave a wrong result (right axis of Fig. 6). This evidence was also found in the case of a monodomain nematic elastomer containing side-chain and main chain nematic polymers in approximately equal proportion [13]: the authors of Ref. [13] concluded that additional internal constraints are imposed by the hairpin folds of long nematic main-chain polymer strands. In such an internally constrained system the relaxation of the elastic modulus is governed by different physical mechanism with respect to the dissipative processes; furthermore, these constraints can prevent the nematic material from reaching its mechanical equilibrium. This explanation can be reasonably applied also to the main-chain nematic elastomer PHBHQ–AA: actually, in this system no plateau of G' was found at the lowest frequencies and the material never reached the equilibrium, making the identification of the longest relaxation time impossible. In the region of the dynamic glass transition, both G' and G'' increase with a power law $G'(\nu) = G''(\nu) \sim \nu^{\xi}$ with $\xi = 0.099 \pm 0.003$. This value is in a good agreement with the power law exponents found in Ref. [13] for those systems with a main chain content which is prevailing over the side chain component.

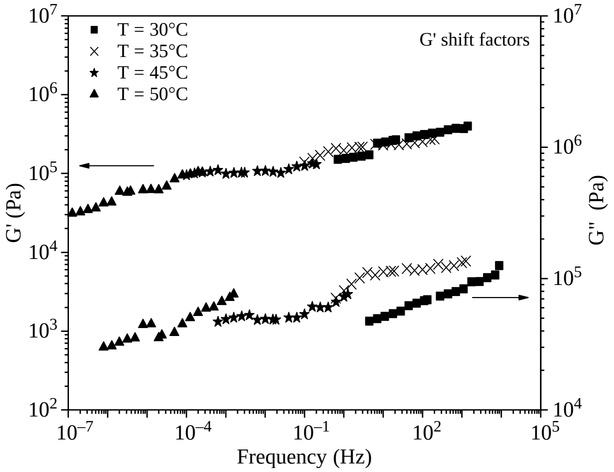

Fig. 5. Master curve of G' of PHBHQ–AA in the nematic phase (left axis) with its optimal shift factors and the corresponding master curve for G'' (right axis) obtained by using the same shift factors. Reference temperature: 50 °C.

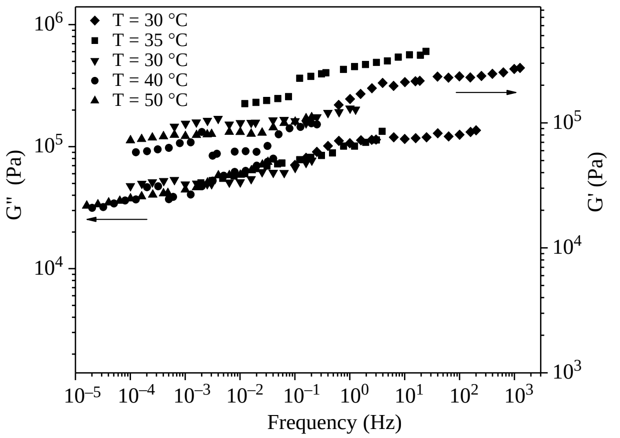

Fig. 6. Master curve of G'' of PHBHQ–AA in the nematic phase (left axis) with its optimal shift factors and the corresponding master curve for G'(right axis) obtained by using the same shift factors. Reference temperature: 50 °C.

In the case of the nematic phase, neither the shift factors used to build the master curve of G' nor the ones used to build the master curve of G'' obey the WLF relationship. It was reported [29] that this could depend on the coupling of the temperature dependence of the viscoelastic response to the temperature dependence of the order parameter.

An increase of the storage modulus of the system in the isotropic phase with respect to the nematic phase can be observed. In a previous paper [24], it was shown that PHBHQ–AA in the nematic phase exhibits a plateau region in the stress–strain curve; moreover, in DMTA experiments a modulus drop appeared in correspondence to the isotropization temperature at the lowest frequency of observation, i.e. 0.1 Hz. These evidences could be explained by the concept of dynamic soft elasticity: in the nematic phase, the underlying director rotations in individual domains, induced by shear, permit to accommodate the imposed strains with a very low elastic response due to relaxation of the internal microstructure. This leads to a reduction in the modulus and a rise in internal mechanical dissipation; above the isotropization temperature, the modulus rises substantially, since the internal relaxation is no longer able to reduce the elastic response (i.e. soft elasticity disappears) [13,27]. However, some authors do not agree with this explanation [14] and they claim that such experimental evidences, as the high internal loss, arise from the presence of interacting bulky groups and can be explained in terms of the de Gennes model [30,31] rather than by the concept of soft elasticity. In their analysis, the SCLCEs reported in the literature can be described as uniaxial rubber networks with a small mechanical anisotropy in the hydrodynamic regime. This is clearly still an open question [14–18], which in the even more complex case of main-chain LCEs, would need a larger amount of experimental evidence, both on chemically different systems and by using a more sophisticated experimental apparatus (e.g. piezo-rheometer), which allows much smaller shear strains and a wider frequency range.

3.2.2. PHBHQ–SA system

This system exhibits a T_g of 36 °C and a smectic A phase up to 87 °C, when it turns isotropic [23]. Fig. 7 reports the master curves for the phase shift ϕ for the sample PHBHQ–SA, obtained from the superposition of measurements taken at 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, 80, 85 °C (smectic A phase) and 90, 95, 100, 105, 110 °C (isotropic phase) and 105 °C as a reference temperature.

Measurements taken at temperatures higher than 110 °C have been discarded because in those cases we got very low values of loss modulus ($<10^3$ Pa), which were in the lower limit of sensitivity of our equipment and, therefore, affected by great error. G'' measurements in the isotropic phase generally gave quite low values (in the range 5–50 kPa), which resulted in a higher uncertainty with respect to the data obtained in LC phase. Of course, phase shift evaluation was also affected. Anyway, we could not get acceptable data superposition in the whole temperature range, whatever the reference temperature chosen, so the data sets corresponding to each phase have been examined separately: the time–temperature superposition does not hold across the smectic–isotropic transition, as it was already reported in the case of SCLCPs, SCLCEs and a slightly crosslinked main-chain smectic polymer [5,9,12,19,29,32,33]. The phase shift increases from ~4° to about 20° throughout the frequency range under examination.

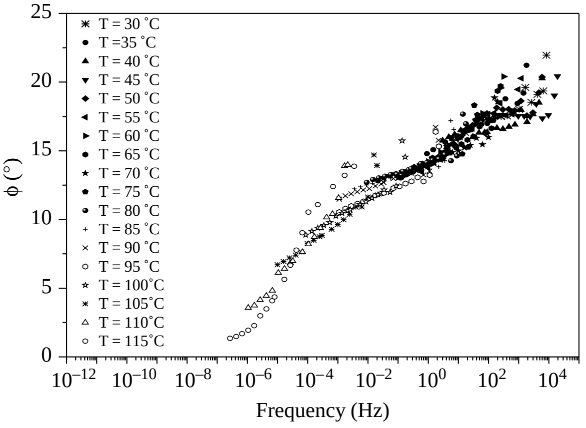

Fig. 7. Master curve for the phase shift ϕ for the sample PHBHQ–SA, obtained from the superposition of measurements taken between 30 and 110 °C. Reference temperature: 105 °C.

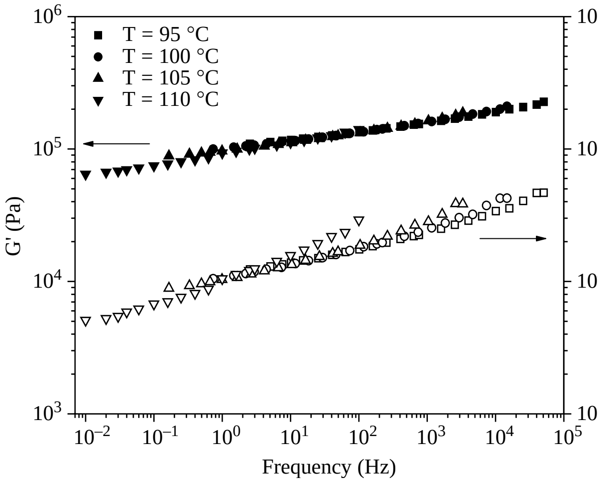

Fig. 8. Master curves of G' (black symbols) and G'' (open symbols) in the isotropic phase of PHBHQ–SA. Reference temperature: 110 °C.

Fig. 8 reports the G' and G'' master curves of PHBHQ–SA in the isotropic phase obtained from experiments performed at 90, 95, 100, 105, 110 with 110 °C as reference temperature. G' increases with a power law $G'(\nu)\sim\nu^{\xi}$, with $\xi=0.080\pm0.001$ and at the lower frequencies seems to approach a plateau value of about 55 kPa. This value is approximately four times lower than G' of the PHBHQ–AA in the isotropic phase (~200 kPa at 10^{-2} Hz). This behavior is in agreement with the result reported in [12], in which an increase in G' is associated with an decrease in the crosslinker length.

G'' increases with a slightly different power law, $G''(\nu)\sim\nu^{\xi}$, with $\xi=0.1$. However, this difference may be not much significant, due to the uncertainty on G'' values at the higher temperatures, which also led to a worse data superposition in the G'' master curve. We remind that in the case of SCLCEs in their isotropic phase, a power law behaviour with an exponent $\xi=0.50$ was reported [5]: in our case, a reasonable explanation for the different behavior can lie in the different composition and structure of the systems under investigation in the present paper. The presence of the mesogen directly incorporated into the main chain seems to increase dramatically the relaxation times of PHBHQ–SA also in the isotropic phase: actually, the hydrodynamic regime is not fully reached even at the lowest frequencies under investigation (10^{-2} Hz). The temperature dependence of the shift factors did not obey the WLF equation; in any case, the data between 90 and 105 °C obeyed an Arrhenius law with an activation energy for flow [28] of about 40 kJ/mol.

Fig. 9 reports the G' and G'' master curves of PHBHQ–SA in the smectic A phase obtained from experiments performed at 40, 45, 50, 55, 60, 65, 70, 75, 80 with 65 °C as a reference temperature. The shift factors used for building the G' master curve produced a quite satisfying superposition also in the case of loss moduli; nevertheless, their temperature dependence did not obey WLF equation.

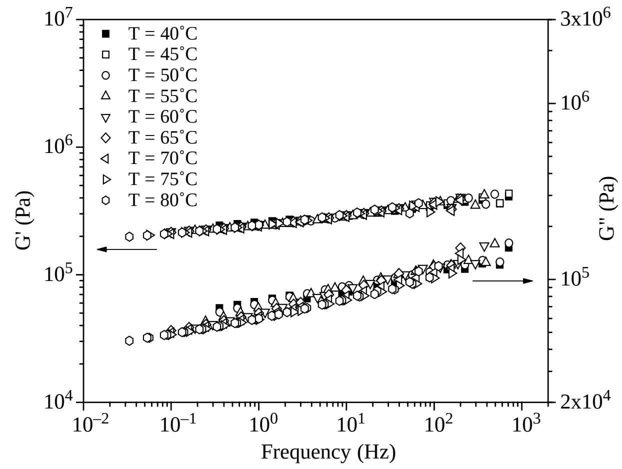

Fig. 9. Master curves of G'(left axis) and G'' (right axis) in the smectic A phase of PHBHQ–SA. Reference temperature: 65 °C.

G' increases with a power law $G'(\nu) \sim \nu^{\xi}$, with $\xi = 0.073 \pm 0.001$. If we assume the validity of this power law over the whole low-frequency regime and we extrapolate the curve $G'(\nu)$ to a value of ∼55 kPa (the approached permanent network plateau value in the isotropic phase), a rough estimate for the lifetime of the longest lived modes of the system $\tau \approx 10^9$ s was obtained. In the case of SCLCEs and SCLCPs in the smectic A phase, a power law with $\xi = 0.3$ was found [5,29] and $\tau \approx 10^5$–10^8 s were estimated. A significant increase in the relaxation time for the smectic PHBHQ–SA sample was also evidenced in uniaxial tension experiments with respect to the nematic PHBHQ–AA system [24]. The drastic lifetime enhancement of the elastic modes in smectic A polydomain SCLCEs was qualitatively explained by the fact that the mesogens linked to a specific polymer backbone usually belong to different smectic layers or even smectic domains. This implies a connection of different polymeric backbones via their side groups in the S_A phase, which gives rise to a transient network structure. This structure, together with the presence of steric hindrance and entanglements, prevents the system from a complete relaxation of the applied stress. In the case of the S_A elastomer under investigation, we can suppose that the presence of mesogens directly incorporated into the main chain gives rise to a more tight transient smectic network where entanglements and steric hindrance play an even more crucial role: this could reasonably lead to longer lifetimes of the elastic modes.

However, it must be pointed out that, in our case, the experiments were performed at temperatures comprised between T_g and ($T_g + 70$ °C), while the experiments reported in the literature for SCLCEs cover the range between ($T_g + 3$ °C) and ($T_g + 100$–120 °C): this is expected to have a different influence on the relaxation times of the systems both in the isotropic and in the smectic A phase.

4. Conclusions

In this paper, we applied the time–temperature superposition (TTS) principle to DMTA analyses in the shear sandwich configuration performed on two main-chain polydomain elastomers, namely PHBHQ–AA and PHBHQ–SA, in their range of linear viscoelasticity. The former exhibits a nematic phase while the latter shows a smectic A phase. We found that TTS did not hold neither across the nematic-isotropic nor the smectic–isotropic transitions, so that data referring to the LC and to the isotropic phases, respectively, were examined separately. An increase of the storage modulus of PHBHQ–AA in the isotropic phase with respect to the nematic phase was observed. This evidence, together with some other previous experimental observations, could be explained in terms of the de Gennes model according to some authors and by the concept of dynamic soft elasticity according to other authors. In general, the presence of the mesogen directly incorporated into the main chain seems to increase the lifetimes of the elastic modes both in the isotropic and in the LC phases, with respect to the SCLCEs. In the case of the smectic A PHBHQ–SA, lifetimes on the order of 10^9 s could be estimated. However, it must be underlined that further experiments should be performed on different types of main-chain LCEs, in order to deduce a more general behaviour of this class of materials and to establish correlations between viscoelastic properties and characteristics of the systems, such as nature of the mesophase, crosslinking density and backbone structure.

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