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Multiscale Structural Characterization of Biocompatible Poly(trimethylene carbonate) Photoreticulated Networks

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Abstract

Poly(trimethylene carbonate) (PTMC) polymeric networks are biocompatible materials with potential biomedical applications. By controlling the chemical synthesis, their functional macroscopic properties can be tailored. In this regard, this work presents the coupling of two experimental techniques: DMA and Solid State NMR,

as an innovative, robust and straight-forward approach to fully characterize the inner structure and its relationship with the macroscopic properties of these PTMC materials. The studied photocured networks had an increasing macromer molecular weight $\overline{M}_n$, varying from 3 kg/mol to 40 kg/mol, which permitted to assess the variation of thermomechanical properties and the Nuclear Magnetic Resonance (NMR) signal decay with this parameter. Dynamic Mechanical Analysis (DMA) showed that the thermomechanical behavior of the PTMC networks depends on the network $\overline{M}_n$. Indeed, the elastic modulus E' and the main α relaxation temperature T_α decrease with PTMC $\overline{M}_n$. Moreover, solid state Multiple Quanta (MQ) 1H NMR investigations demonstrated that the network crosslink density is also linked to this chemical parameter. Interestingly, both techniques showed for the 40 kg/mol PTMC a neat difference of the effect of the chemical crosslinks and the physical entanglements on the materials network structure and thermomechanical behavior. Specifically two different molecular relaxation domains were highlighted, which are not observed for the rest of the studied materials. By utilizing DMA and solid state NMR in a complementary and synergetic manner, this work provides a novel and robust approach of determining and better understanding key structure-property relationships, specifically the inner structure and macroscopic properties, of such functional polymers.

Keywords

Double-Quantum DQ 1H NMR, Dynamic Mechanical Analysis, Biocompatible polymers, Tough networks, Network morphology, Thermomechanical properties, Structure-properties relationship.

Introduction

Poly(trimethylene carbonate) (PTMC) is a biodegradable, amorphous and flexible polymer with potential biomedical applications because of its biocompatibility and biodegradability.

As such, most of the research on this polymer has been focused on in-vivo drug-delivery applications.¹⁻¹⁵ Moreover, by photo-crosslinking methacrylated PTMC oligomers (macromers), tough, tear-resistant networks can be obtained. Because of this, in the past few years there has been a growing interest on the use of these networks as bulk materials.^{12,16-21} Networks prepared from macromers with molecular weights of 10 kg/mol and higher were shown to be rubber-like with high tensile strength, toughness, and tear resistance at room temperature.^{12,16-21} Due to these properties, PTMC-based photo-crosslinked networks have been investigated for application as meniscus implants,¹⁷ bone implants²⁰ and micro-vascular networks.²¹ The applicative functionality of PTMC networks depends largely on their mechanical behavior.^{16,17} It was shown that the mechanical properties of PTMC networks strongly depend on the crosslink density, *i.e.* the network morphology, as well as from the macromer chain length.¹⁶ Hence in order to fully understand the influence of the inner structure on PTMC macroscopic properties, the thermomechanical behavior and structural morphology of these networks need to be fully studied.

In this regard, Dynamic Mechanical Analysis (DMA) has been extensively used to study the thermomechanical behavior of polymers through a macroscopic approach, and can be considered to be a primary characterization technique in polymer science.^{22,23} DMA measurements were thus undertaken in this work in order to study the evolution of the molecular mobility, namely the main α relaxation temperature, the elastic moduli E' , and the mechanical crosslink density of PTMC networks with varying macromer molecular weight.

Such characterizations were completed by time-domain NMR analyses. This technique has proven to be a powerful tool to characterize the structure, morphological organization and molecular mobility of polymers.²⁴⁻²⁷ Amongst these analyses, pseudo-solid 1H echoes have been used to describe polymeric networks.²⁸⁻³⁵ In particular, Double-Quantum DQ 1H sequences have been successfully used in elastomeric-like polymer networks (*i.e.* natural & synthetic rubbers and PDMS^{36,37}) and, through a careful data treatment, have allowed the fine study of the networks structure and dynamics, namely the polymers' molecular mobility,

crosslink density v_C , and chain defects concentration w_{def} ,^{36–47} as well as the evolution of such network properties with temperature,^{48,49} chemical modification^{50–52} and thermal ageing.^{53,54} The common basis of these approaches is their potential ability to discriminate dynamical and structural effects, which allows semi-local structural features of networks to be retrieved from local dynamical measurements.

This manuscript aims to demonstrate that for functional polymeric networks such as PTMC, it is of main importance to fully characterize and comprehend their intrinsic structure. Such an investigation allows the insight to chemically tailoring their structure, allowing a better control of specific macroscopic properties. This study was carried out by combining a macroscopic method with a molecular-scale technique (i.e. DMA & MQ 1H NMR respectively). This robust scientific approach has seldom been described in the literature and specifically, it has not been carried out for PTMC networks. By studying these polymers of different macromer molecular weights, the influence of the inner network structure can be thoroughly and precisely described.

Materials

Trimethylene carbonate (TMC) monomer was obtained from Huizhou ForYou Medical Devices Co. (China). Trimethylol propane (TMP), tin(II) 2-ethylhexanoate ($Sn(Oct)_2$), methacrylic anhydride, hydroquinone and triethylamine were purchased from Sigma (USA) and used as received. Dichloromethane and chloroform were purchased from Merck (Germany). TPO-L (2,4,6-trimethylbenzoylphenyl phosphinate) was obtained from Carbosynth Limited (United Kingdom). Ethanol was purchased from Altia oyj (Finland).

Macromer synthesis

To obtain three-armed, hydroxyl-terminated PTMC oligomers, ring opening polymerization reactions of TMC were performed at 130°C under nitrogen atmosphere using TMP as initia-

tor and $\text{Sn}(\text{Oct})_2$ as catalyst. By adjusting the monomer to initiator molar ratio oligomers with different molecular weights $\overline{M}_n$ could be prepared. The targeted $\overline{M}_n$ were 3, 10, 17.5, 25 and 40 kg/mol.

The polymerization reaction was performed for 3 days. The oligomers were subsequently dissolved in dichloromethane (2 mL/g oligomer) and functionalized with methacrylic anhydride (7.5 mol/mol oligomer) in the presence of triethylamine (7.5 mol/mol oligomer) and hydroquinone (0.1 wt% relative to the monomer). After 5 days, the methacrylate functionalized oligomers (macromers, PTMC-tMA) were precipitated in cold ethanol and dried at 40°C under vacuum for 1 week. The $\overline{M}_n$ of the obtained oligomers, the monomer conversion and the degree of functionalization were determined by ^1H -NMR as described previously.¹⁷ Briefly, the molecular weight was determined by comparing the area of the $-\text{CH}_3$ initiator peak at $\delta = 0.92\text{ppm}$ with the area of the PTMC methylene peak at $\delta = 4.24\text{ppm}$. The conversion is calculated by comparing the TMC monomer peak at $\delta = 4.45\text{ppm}$ with the area of the PTMC methylene peak at $\delta = 4.24\text{ppm}$. The degree of functionalization is determined by comparing the $-\text{C}=\text{CH}_2-$ ^1H signals at $\delta = 5.58\text{ppm}$ and $\delta = 6.13\text{ppm}$ of the methacrylate groups with the $-\text{CH}_3$ initiator peak at $\delta = 0.92\text{ppm}$.

Network preparation

To obtain crosslinked networks, the macromers were dissolved in chloroform. The chloroform solutions contained 20-40 wt% PTMC macromers. To these solutions, 5 wt% (relative to the macromers) of TPO-L photoinitiator was added. The solutions were cast in Teflon molds (50x25 mm) and the solvent was allowed to evaporate overnight. The macromers were then crosslinked at room temperature under nitrogen in a home-made crosslink box for 1h at 395-405 nm at an intensity of 1 mW/cm^2 . The obtained networks were subsequently post-cured under visible light for 40 minutes at room temperature. As these networks have a functionality $f = 3$, the theoretical chemical crosslink density v_{chem} of such networks can be calculated as $= 1/(3 \times \overline{M}_n)$. The reaction mechanism is shown in Figure 1.

Figure 1: Reaction mechanism and chemical structure of a three-armed PTMC macromer prepared by the ring opening polymerization of TMC using TMP as initiator.¹⁶

Experimental Methods

Swelling characterization

The volume degree of swelling at equilibrium q and the gel content w_{swell} were determined in triplicate at room temperature by swelling rectangular shaped specimens (5x5x0.5mm) in chloroform for 24 hours, which was enough time to reach solvent sorption equilibrium. The q and w_{swell} values were calculated from Equations 1 and 2 respectively.

$$q = 1 + \left(\frac{m_{swollen} - m_{dry}}{m_{dry}} \right) \left(\frac{\rho_P}{\rho_S} \right) \quad (1)$$

$$w_{swell} = \frac{(m_{initial} - m_{dry})}{m_{initial}} \times 100\% \quad (2)$$

where $m_{swollen}$ is the mass of the swollen networks, m_{dry} the mass of the insoluble part of the networks after drying, $m_{initial}$ the initial mass of the networks, and ρ_P and ρ_S the densities of PTMC ($=1.31 \text{ g/cm}^3$)¹⁶ and chloroform ($=1.48 \text{ g/cm}^3$) respectively.

DSC measurements

The thermal properties of the obtained macromers and networks were determined by Differential Scanning Calorimetry (DSC) using a TA instruments Q2000. Samples weighing 5-10 mg were heated from -60°C to 100°C at 10°C/min and subsequently cooled to -60°C at 50°C/min. After 5 minutes a second heating scan was performed, from which the glass transition temperatures T_g were determined. Temperature calibration was performed using indium as a calibration standard.

DQ 1H Solid State NMR Measurements

Elastomer networks, and more generally entangled polymer melts, are characterized by the presence of topological restrictions due to both crosslinks and entanglements which restrict

reorientational motions of chain segments and introduce local anisotropy along chains. At high temperatures relative to T_g , intrachain motions are very fast compared to NMR time scales and the effect of the local anisotropy can be expressed as a separate factor contributing to the relaxation signal.³⁰ In this regime the NMR relaxation function can be expressed according to Equation 3.^{30,33}

$$\frac{M(t)}{M_0} = \exp\left(-\frac{t}{T_2}\right) \langle \cos(\Delta_R t) \rangle \quad (3)$$

where T_2 is the spin-spin or transverse relaxation time and $\langle \cos(\Delta_R t) \rangle$ is a term that comprises the non-zero residual dipolar interaction due to local anisotropic chain segment motions. Brackets denote the ensemble average over all polymer chains.

It follows that in entangled or crosslinked polymers, the overall transverse relaxation function has a generally complex, non-exponential form, with a so-called "*pseudo-solid*" behavior.³⁰ It is the residual dipolar interaction factor $\langle \cos(\Delta_R t) \rangle$ which contains the structural information, as the local anisotropy of chain segment motions is related to the network structure. One difficulty is that both the $\exp(-t/T_2)$ and $\langle \cos(\Delta_R t) \rangle$ terms often have comparable relaxation time rates. Special techniques have thus been developed to discriminate those terms, *i.e.* isolate the structural information.

The *Double-Quantum* (DQ) time-domain NMR method developed by Saalwächter^{36,37,41–44,46–49,54} based on an improved Baum - Pines^{39,40} pulse sequence, and utilized in this work, is a convenient way to achieve this discrimination, and it has been widely used to characterize the structure of the elastic network (*i.e.* chains possessing crosslinks and/or entanglements) in elastomers.

$DQ\ ^1H$ measurements were performed using a Bruker Avance III MAS 2 400 MHz NMR spectrometer equipped with a 5mm 1H static probe. Samples were finely cut to fit in the rotor and tested at different temperatures above their T_α measured by DMA. $DQ\ ^1H$ experiments were thus based on the aforementioned pulse sequence. DQ -NMR experiments using the Baum and Pines/Saalwächter sequence, yield two components as a function of the

DQ evolution time $2\tau_{DQ}$: the DQ buildup I_{DQ} and the reference decay I_{REF} , which are exemplified in Figure 2.

Figure 2: MQ 1H NMR I_{ref} , I_{DQ} , $I_{ref} - I_{DQ}$, and I_{def} signals obtained for the PTMC $10k$ network at $T_\alpha + 90^\circ\text{C}$. The contribution from defects I_{def} is emphasized in the $I_{ref} - I_{DQ}$ signal as the fraction of the signal with a long relaxation time (dashed black curve). Extrapolation of the I_{def} signal to $\tau_{DQ} = 0$ gives the fraction of defects w_{def} .

The I_{ref} signal contains the contribution from all quantum orders except that of the DQ contribution, so that the sum $I_{ref} + I_{DQ}$ is the relaxation signal from which all dipolar contributions have been refocused. In other words it contains only the contribution from the chain dynamics. This signal comprises the response of both the dipolar coupled network, which relaxes faster and in a non-exponential manner, and of the uncoupled mobile defects such as pendant and/or free chains, which exhibit a slower exponential relaxation. By normalizing the DQ contribution according to Equation 4, only the structural contribution to the relaxation is retained.

$$I_{nDQ} = \frac{I_{DQ}}{I_{ref} + I_{DQ}} \quad (4)$$

In the vicinity of T_g , crosslinked and entangled polymers undergo complex dynamics with widely spread relaxation time distributions, corresponding to motions at different scales. In

this regime, structural and dynamical contributions may not be expressed as two distinct factors, as it was illustrated in Equation 3. Then the separation of both effects is not straightforward. In order to determine at which temperature the DQ NMR signals, and thus the structural effect, become independent of temperature, PTMC $3k$ networks were analyzed from $T_\alpha + 50^\circ\text{C}$ to $T_\alpha + 100^\circ\text{C}$ every 10°C . This range of temperatures was chosen so as to have networks with theoretical elastomeric behaviors (*i.e.* $T + 50^\circ\text{C}$ equal or above the glass transition temperature $T_g(\text{DSC})$ or $T_\alpha(\text{DMA})$ ⁵⁵).

Figure 3: I_{nDQ} normalized signal obtained from Equation 4 as a function of τ_{DQ} for the PTMC $3k$ network at different temperatures.

The effect of temperature is illustrated in Figure 3. This graph represents the normalized DQ signal I_{nDQ} computed from Equation 4 described above as a function of τ_{DQ} . It is seen that the I_{nDQ} signal changes and increases as temperature increases. Moreover, this I_{nDQ} signal becomes independent at temperatures of and above 70°C , which corresponds to $T = T_\alpha + 80^\circ\text{C}$ or above. This regime corresponds to the high temperature regime mentioned above, in which the normalized DQ signal reflects solely the structure of the network. Below this regime and as temperature comes closer to T_g , complex segmental motions take place at time scales comparable to the delay between pulses in the DQ pulse sequence, which impair

the efficiency of the sequence to refocus dipolar interactions and select DQ contributions. This is the reason why the overall amplitude of the normalized signal decreases drastically as temperature decreases, as it is observed in Figure 3.

In the temperature-independent regime, the normalized DQ signal originating from the network structure alone must reach the theoretical relative value of 0.5 in the long τ_{DQ} limit.^{52,56} To achieve this, it is necessary to eliminate the contribution of "defects", *i.e.* non-elastic chains (pendant and free chains). Although the full magnetization equals $I_{ref} + I_{DQ}$, a heuristic manner to easily identifying and subtracting the defects contribution I_{def} is to consider the $I_{ref} - I_{DQ}$ signal^{43,52} which is shown in Figure 2. I_{def} was determined by fitting a double exponential on the long-time domain of the magnetization signal. The percentage of defects w_{def} was obtained by extrapolating this contribution to $\tau_{DQ} = 0$, as it is also shown in Figure 2. The normalized DQ signal excluding the non-elastic chains contributions was then calculated from Equation 5:

$$I_{nDQ} = \frac{I_{DQ}}{I_{ref} + I_{DQ} - I_{def}} \quad (5)$$

DQ signals for the PTMC 3k network characterized at temperatures equal to 70°C, 80°C, and 90°C ($T_\alpha + 80^\circ\text{C}$, $T_\alpha + 90^\circ\text{C}$, and $T_\alpha + 100^\circ\text{C}$ respectively) were then normalized by using Equation 5. The computed I_{nDQ} signals were then plotted as a function of τ_{DQ} . These results are shown in Figure 4.

It is seen in Figure 4 that the I_{nDQ} relative amplitude of 0.5 is obtained for the three considered temperatures. In detail, the I_{nDQ} signal at 70°C does not exactly superpose with the I_{nDQ} signals obtained at 80°C and 90°C. This means that at 70°C, the I_{nDQ} normalization is still a little dependent on the temperature. However, for temperatures equal or higher than 80°C for the PTMC 3k network (*i.e.* $T_\alpha + 90^\circ\text{C}$ and above), the I_{nDQ} normalized signals superpose well with each other (*i.e.* independent of temperature).

Hence, *in this work all of the PTMC networks were studied at $T_\alpha + 90^\circ\text{C}$ with the I_{nDQ} signals being computed using Equation 5.* This ensured that the samples were tested at the

Figure 4: I_{nDQ} normalization signal obtained from Equation 5 as a function of τ_{DQ} for the PTMC 3k network at different temperatures.

temperature-independent DQ NMR regime while assuring that all the PTMC networks possessed the same state of molecular mobility. A detailed study on the influence of temperature on the NMR relaxation for these materials will be discussed in a forthcoming article.

Moreover, I_{nDQ} gives access to the residual dipolar coupling D_{res} related to the network structure. In turn the local average dynamic segmental orientation parameter S_b is deduced using Equation 6, in which D_{stat} is the static coupling constant, D_{res} the residual dipolar coupling and k a correction factor related to intersegmental motions. The key point is that S_b is directly related to the intrinsic structure of the polymer network *via* R , the average end-to-end vector between crosslinks or equivalently *via* N , the number of statistical segments between crosslinks. b is the statistical segment length. By considering that $R^2 = Nb^2$ as for ideal chains, S_b should be proportional to $1/N$, or equivalently to the crosslinks density $v_C = 1/M_C$ as detailed in Equation 6.

$$S_b = k \frac{D_{res}}{D_{stat}} \approx \frac{R^2}{N^2 b^2} \approx \frac{1}{N} \propto \frac{1}{M_C} \propto v_C \quad (6)$$

In this work the values for k and D_{stat} were not obtained quantitatively. As these factors should be identical in all samples in the series, measuring D_{res} values allows quantitative comparison between the different networks. To obtain the D_{res} value for each polymer characterized at $T_\alpha + 90^\circ\text{C}$, the I_{nDQ} signals were fitted by a function detailed in Equation 7, up to $I_{nDQ} = 0.48$:

$$I_{nDQ} = 0.5 [1 - \exp(-D_{res}\tau_{DQ})^n] \quad (7)$$

where n is an exponent varying between 1 and 2. The closer n is to the value of 2, the more homogeneous the network is. [Figure SI.1 \(*Supporting Information*\)](#) shows an example of such a fit for the PTMC 10k network characterized at $T_\alpha + 90^\circ\text{C}$.

Dynamic Mechanical Analysis

Dynamic Mechanical Analyses were performed on a TA Instruments Q800 DMA operating in tensile mode. PTMC films were cut into ISO 527-4b dogbone-shaped specimens with operational dimensions of $18 \times 2 \times 0.7\text{mm}^3$. These samples were heated from -140°C to 180°C with a heating rate of $3^\circ\text{C}/\text{min}$ and analyzed with a frequency of 1 Hz, a pre-strain of 0.01%, and strain of 0.1%. The main α relaxation temperature T_α was obtained from the half-height point of E' drop corresponding to this relaxation.⁵⁷

Furthermore, the crosslinking density v_{C-DMA} for each PTMC network was obtained by conducting a DMA strain sweep measurement at $T_\alpha + 90^\circ\text{C}$ so as to allow a precise comparison between these results and those obtained by NMR at the same molecular mobility state. The linear regime was thus determined by plotting the storage modulus E' as a function of the strain ϵ and the value of E' was taken from the linear regime plateau. Then, the crosslinking density v_{C-DMA} was calculated according to Equation 8.²²

$$v_{C-DMA} = \frac{E'}{\phi RT f} \quad (8)$$

where R is the ideal gas constant = $8.314 \text{ J/mol} \cdot \text{K}$, $T=T_{\alpha} + 90^{\circ}\text{C}$, f is the network functionality which for PTMC samples is equal to 3, and ϕ is a factor linked to the network model. For the *affine* model⁵⁸ $\phi = 1$, whereas for the *phantom* model⁵⁹ $\phi = \frac{f-2}{f}$. In this work, two series of v_{C-DMA} values were thus calculated according to both the affine and phantom models.

Results and Discussion

Three-armed, methacrylate functionalized PTMC oligomers (macromers) were prepared *via* the ring opening polymerization of TMC and subsequent functionalization with methacrylic anhydride. Figure 1 shows the chemical structure of a PTMC macromer. By adjusting the monomer to initiator ratio, oligomers with different molecular weights were obtained. Table 1 shows the obtained molecular weights as confirmed by High Resolution ^1H -NMR in solution in DMSO. Subsequent functionalization yielded macromers with a degree of functionalization $\geq 86\%$. Then, characterization of the macromers by DSC indicated that the materials had a T_g between -21°C and -14°C as shown in [Figure SI.2 \(Supporting Information\)](#). It is observed that the macromers T_g slightly increases with increasing molecular weight, though within experimental error deviation range. The values are summarized in Table 1.

Table 1: Physico-chemical properties of the obtained macromers.

Intended $\overline{M}_n$ (g/mol) $\times 10^3$	Obtained $\overline{M}_n$ (g/mol) $\times 10^3$	Conversion (%)	Functionality (%)	T_g ($^{\circ}\text{C}$)
3	3.4		96	-21.2
10	10		100	-15.9
17.5	16.7	99	100	-16.3
25	25.2		100	-15.3
40	36.6		86	-14.5

The obtained PTMC networks were similarly characterized by and by swelling in chloroform for 24 hours. Table 2 provides an overview of these properties. All networks exhibited a T_g of approximately -15°C as shown in Figure 5a. The gel contents w_{swell} of the networks

Figure 5: (a) DSC Thermograms highlighting the T_g and (b) Storage modulus E' obtained for all PTMC networks as a function of temperature.

were found to be between 70 and 93%, with the lowest w_{swell} for the network prepared from the PTMC 40k macromer, *i.e.* with the highest molecular weight. This result is similar to that previously reported by Schüller-Ravoo et al.¹⁶ It was also found that the degree of swelling q of the networks in chloroform (summarized in Table 2) increased with macromer molecular weight, as was expected since networks with a lower crosslink density are able to swell more.

Figure 5b displays the obtained storage mechanical modulus E' as a function of temperature obtained by DMA for each PTMC as a function of temperature. The loss modulus E'' is shown in Figure SI.3 (*Supporting Information*). Such plots allowed to deepen the understanding as regards the molecular mobility and thermomechanical properties of PTMC networks at or below T_α .

It is seen in Figure 5b that the elastic modulus E' below T_α diminishes when the macromer molecular weight increases. Then, from Figure 5b, the α relaxation temperatures T_α (comparable to the T_g obtained by DSC) were obtained and are listed in Table 2. Interestingly, contrary to the T_g values obtained by DSC, the T_α diminishes with the macromer molecular weight, a trend that is in line with previously reported T_g values for PTMC networks.¹⁶ The

difference of results given by the two techniques can be attributed to the fact that DMA is more sensible to the physical and chemical crosslink density when compared to the DSC, which probes mostly the molecular mobility. Thus, the aforementioned result is expected because if the distance between reticulation nodes increases, the polymer chains within the network are less constrained by the nodes and thus their relaxation movements can be activated at lower temperatures. This would also lead to a more heterogeneous material. Indeed, [Figure SI.3 \(Supporting Information\)](#) shows that the α relaxation peak becomes broader as the PTMC molecular weight increases. In particular, the PTMC 40k network would seem to possess either a very large T_α or a shouldering towards higher temperatures corresponding to a second α relaxation. This network has a larger α relaxation temperature distribution ΔT_α (taken at half-height) by *ca.* 5°C than those of the other networks as listed in Table 2. These phenomena could be due to the presence of a different network structure in this PTMC sample that is different from the rest of the materials. This will be further discussed with the 1H MQ NMR results, as they can provide an additional insight on the networks structure.

Furthermore, it is seen in Table 2 that the crosslink densities obtained from swelling experiments v_{C-chem} ($= 1/(3 \times \overline{M}_n)$) and by DMA v_{C-DMA} evolve similarly according to the molar mass of the PTMC macromers. In detail, the v_{C-chem} values are fairly similar to those of v_{C-DMA} obtained by the affine model, with v_{C-DMA} being slightly higher than v_{C-chem} . This difference would be a first indicator of a presence of not only chemical crosslinks but also chain entanglements that would behave as physical nodes. Moreover, the v_{C-DMA} values calculated from the phantom model are *ca.* three times larger than those of v_{C-chem} . This might mean that the PTMC networks may be better described by the affine model.

Concerning the MQ 1H NMR measurements, Figure 6a shows the I_{nDQ} signals after normalization with Equation 5, as a function of τ_{DQ} for all studied PTMC networks at $T_\alpha + 90^\circ\text{C}$. It is observed that the evolution of the I_{nDQ} buildup is different for all samples, becoming steeper when the molar mass of the network decreases, *i.e.* when the crosslink

Table 2: Physico-chemical, DSC, DMA, and MQ 1H NMR results obtained for the studied PTMC networks.

PTMC	Physico-chemical			DSC	DMA			MQ 1H NMR				
	w_{swell} (%)	q (%)	v_{C-chem} (mol/g) $\times 10^4$	T_g ($^{\circ}C$)	T_{α} ($^{\circ}C$)	ΔT_{α} ($^{\circ}C$)	E' @ $T_{\alpha} + 90^{\circ}C$ (MPa)	v_{C-DMA} affine phantom (mol/g) $\times 10^4$	$D_{res}/2\pi$ (Hz)	w_{def} (%)	n	
3k	8.6 ± 0.6	2.8 ± 0.1	8.82	-16.0	-10	9	10.7	12.15	36.44	441.4	9.5	1.54
10k	8.8 ± 0.2	4.4 ± 0.1	3.00	-13.5	-11	11	4.8	5.46	16.39	272.7	12.7	1.62
17.5k	7.3 ± 0.2	5.3 ± 0.2	1.80	-14.0	-16	11	3.5	4.04	12.13	231.4	8.9	1.62
25k	15.8 ± 0.5	8.9 ± 0.1	1.20	-14.8	-16	7	1.5	1.73	5.20	181.4	20.9	1.55
40k	30.9 ± 0.5	17.1 ± 0.6	0.81	-15.1	-18	15	1.2	1.39	4.18	172.1	28.1	1.42

density increases. An analogous result was observed by Vieyres *et.al.*⁵² for natural rubbers with different crosslink densities.

Furthermore, from the I_{nDQ} normalization calculations, the percentage of defects (*i.e.* chains not participating in the network) w_{def} was also obtained. These values are also listed in Table 2. These values are similar to those obtained by swelling experiments (w_{swell} , found in Table 2). This shows that the results given by NMR structural measurements are comparable to macroscopic physico-chemical tests and that they are quantitative.

The residual coupling constant D_{res} was subsequently obtained by fitting the I_{nDQ} signals with Equation 7. The obtained values are found as well in Table 2. *It must be recalled that D_{res} does not give the crosslink density but is proportional to it (see Equation 6).* It can be seen that the D_{res} values decrease when the macromer molar mass increases, which means that the NMR crosslink density v_{C-NMR} , *which could be extracted from D_{res} according to Equation 6, would decrease accordingly with* the molar mass of the PTMC macromers, meaning that when the length of the macromer increases, the amount of crosslinks in the material decreases. These results are again in good agreement with those observed by macroscopic characterizations, *i.e.* DMA analyses, and also perfectly coherent with expectation.

All I_{nDQ} signals were plotted as a function of the reduced $D_{res}\tau_{DQ}$ time (*i.e.* a normalization of τ_{DQ} by D_{res}) for each PTMC network. This plot is shown in Figure 6b. It is seen that all I_{nDQ} signals superpose nearly perfectly with each other. This means that the different PTMC samples have in fact the same network morphology in terms of the homogeneity of the crosslink density. Accordingly, the values of the fitting parameter n are quite similar in all samples. Thus the only intrinsic structural difference between the PTMC studied samples is the crosslink density v_C .

It has to be noted that in the case of the PTMC 40k network, although it superposes fairly well with the rest of the networks in the I_{nDQ} *vs.* $D_{res}\tau_{DQ}$ plot shown in Figure 6b, there seems to be two different slopes at the beginning and at the end of the curve in comparison with the other networks. Saalwächter *et.al.* have reported and discussed

Figure 6: (a) I_{nDQ} values as a function of τ_{DQ} for all PTMC networks obtained by MQ 1H NMR measurements at $T_\alpha + 90^\circ C$, and (b) same plot with a normalization of τ_{DQ} by D_{res} .

similar behavior in bimodal PDMS elastomer samples.⁴¹ For the studied PTMC 40k network, this behavior originates from two different chain populations with slightly different local orientational order, which in the present context should be interpreted as slightly different crosslink densities.

To analyze this curve in more details, the PTMC 40k network I_{nDQ} vs. τ_{DQ} signal was fitted with Equation 7 with two distinct contributions, the first one covering the range $0 \leq I_{nDQ} \leq 0.25$ and the second one covering the range $0.25 \leq I_{nDQ} \leq 0.48$. The obtained D_{res} and n values are listed in Table 3 and are compared to those previously obtained for this network with a single chain relaxation distribution domain.

Table 3: D_{res} and n values obtained from Equation 7 for PTMC 40k networks considering a single or two chain relaxation distribution domains.

I_{nDQ} Fit		$D_{res}/2\pi$ (Hz)	n
Single Distribution	-	172.1	1.41
Double Distribution	$0 \leq I_{nDQ} \leq 0.25$	183.7	1.49
	$0.25 \leq I_{nDQ} \leq 0.5$	161.6	1.59
Average	-	172.7	1.54

It is observed in Table 3 that the D_{res} value for the first chain population domain (*i.e.* $0 \leq I_{nDQ} \leq 0.25$) is slightly higher than that for the second domain (*i.e.* $0.25 \leq I_{nDQ} \leq 0.48$). Moreover, their average value is fairly equal to the D_{res} value previously obtained by fitting the whole PTMC 40k network I_{nDQ} *vs.* τ_{DQ} signal. The single and double relaxation distribution fits obtained from Equation 7 are shown in Figure 7. These fits are superposed to the experimental I_{DQ} *vs.* τ_{DQ} plot for the PTMC 40k network.

Figure 7: Single and double relaxation distribution fits obtained from Equation 7 for PTMC 40k networks superposed to the I_{nDQ} *vs.* τ_{DQ} experimental signal.

It can be seen in Figure 7 that the fit considering a *double* relaxation distribution domain better follows the experimental PTMC 40k plot when compared to the *single* distribution fit. These results confirm the hypothesis regarding the existence of two chain populations or two domains corresponding to slightly different crosslink densities in the PTMC 40k network.

The obtained D_{res} values were plotted as a function of the chemical v_{C-chem} crosslink density as shown in Figure Figure SI.4 (*Supporting Information*). It is important to note that for the PTMC 40k sample, the *average* D_{res} listed in Table 3 was considered. Figure SI.4 shows clearly a good, nearly linear correlation between D_{res} and v_{C-chem} with a non-zero intercept at v_{C-chem} extrapolated to 0. This means that the crosslink density determined

from NMR would be a non-zero when extrapolated to zero chemical crosslinking, and this can be attributed to the physical entanglement contribution to D_{res} . When the elastic modulus E' at $T_\alpha + 90^\circ\text{C}$ is plotted as a function of the chemical crosslink density v_{chem} as shown in Figure SI.5 (*Supporting Information*), a similar nearly linear correlation between E' and v_{C-chem} exists. The contribution of physical entanglements is much lower however. One may even argue that the extrapolated value at $v_{C-chem} = 0$ would be close to zero. This difference between the behavior of D_{res} and E' may originate in the difference in time scales of both measurements. Indeed, the NMR measurements probe the response of the network over a time scale of a few microseconds. Physical entanglements or some other topological constraints may then be active on this time scale, while they have relaxed on the DMA time scale.

Then, the D_{res} values were plotted as a function of the DMA v_{C-DMA} crosslink densities obtained either from the affine or phantom models. These results are shown in Figure 8.

Figure 8: D_{res} values obtained by MQ ^1H NMR measurements as a function of DMA v_{C-DMA} crosslink densities calculated either from the *affine* model or *phantom* model for all studied PTMC networks. The dashed lines are linear fits and serve as a guide for the eyes.

It is seen in Figure 8 that a linear relationship between the crosslink density v_{C-DMA} for both the affine and phantom models and D_{res} . This was expected from rubber elastic-

ity theory,^{60,61} and from the affine,⁵⁸ phantom,⁵⁹ and junction affine^{62–64} network models themselves. This is attributed to both NMR and DMA being capable of probing the chemical network, as well as chain entanglements acting as physical crosslinks. According to the rubber elasticity theory,^{60,61} if a pure chemically-crosslinked network with no entanglements is considered, the value at the y-intercept of the D_{res} vs. v_C plots should be zero, since the chemical crosslink density of a non-crosslinked polymer would be non-existent. In this study a non-zero y-intercept value was obtained. A similar result was found by Vieyres *et.al.*⁵² for natural rubber, and was attributed to physical entanglements.

In the case of the studied PTMC materials, the existence of physical entanglements is highly probable. Indeed, the PTMC macromer molecular weight $\overline{M}_n$ is much larger than the PTMC repeating unit molecular weight $M_0 = 102 \text{ g/mol}$. For instance, for the PTMC 3k network the $\overline{M}_n/M_0$ ratio is of *ca.* 30 and for the PTMC 40k network it is of *ca.* 400. Thus, chain entanglements would be able to exist within the macromers before the formation of chemical crosslinks. More importantly, some trapped entanglements may be formed during the PTMC macromer photoreticulation. The amount of such trapped entanglements may in fact increase as the chemical crosslink density increases, as reflected by the non-linear variation of both E' and D_{res} at small v_{Cchem} values in Figures SI.4 and SI.5 (*Supporting Information*). Moreover, Figure 8 shows that DQ NMR measurements are more sensitive to physical entanglements than DMA analyses.

Altogether these results show that the physical chain entanglements characterized herein by DQ 1H NMR and DMA have also an important contribution to the thermomechanical behavior of PTMC materials when compared to the chemical crosslink network. This is specifically true in the case of PTMC 40k networks, as their chemical crosslink density v_{Cchem} is small, thus the presence of physical entanglements reinforces the thermomechanical properties of this network.

Conclusion

This study has demonstrated the pertinence of combining a multiscale approach to characterize a series of homogeneous crosslinked PTMC networks by DMA analyses and $DQ\ ^1H$ Solid State NMR measurements. It is established herein that the results yielded by both experimental methods complement well each other and allow a fine study of a polymer network structure and its influence on its macroscopic thermomechanical properties. Specifically, it was confirmed that the studied PTMC networks, having different macromer molar masses, possess the same intrinsic chemical and physical network morphology. The only difference between them is their crosslink network densities, which are due to the different macromer molar masses. Moreover, it was demonstrated by both DMA and NMR measurements that chain entanglements acting as physical crosslinks are also present in such PTMC networks and their concentration as well as their effect on the thermomechanical behavior of these materials can be quantifiable. The results obtained in this work allow a better understanding of PTMC materials and the tailoring of their properties to enhance their potential use in biocompatible applications, achieved by combining DMA and solid state NMR through a robust scientific approach. This concept will be further extended to assess the influence of temperature as well as the chemical synthesis procedure on the PTMC network structure and their functional macroscopic properties. Finally, this work has shown that such a study can be readily undertaken on similar elastomeric-like functional polymeric networks.

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Supporting Information

Figure SI.1: I_{nDQ} signal obtained for the PTMC 10k network at $T_{\alpha} + 90^{\circ}\text{C}$ fitted by Equation 7.

Figure SI.2: DSC Thermograms highlighting the T_g obtained for PTMC macromers.

Figure SI.3: Loss modulus E'' obtained for all PTMC networks as a function of temperature.

Figure SI.4: D_{res} values obtained by MQ 1H NMR measurements as a function of the chemical v_{C-chem} crosslink densities for all studied PTMC networks. The dashed line is a linear fit and serves as a guide for the eyes.

Figure SI.5: E' at $T_{\alpha} + 90^{\circ}C$ obtained by DMA as a function of the chemical v_{C-chem} crosslink density. The dashed line is a linear fit and serves as a guide for the eyes.

References

- (1) Zhu, K.; Hendren, R.; Jensen, K.; Pitt, C. Synthesis, Properties, and Biodegradation of Poly (1,3-trimethylene carbonate). *Macromolecules* **1991**, *24*, 1736–1740.
- (2) Albertson, A.-C.; Sjöling, M. Homopolymerization of 1,8Dioxan-2-one to High Molec-

ular Weight Poly(Trimethylene Carbonate). *Journal of Macromolecular Science* **1992**, *29*, 43–54.

- (3) Albertson, A.-C.; Eklund, M. Influence of molecular structure on the degradation mechanism of degradable polymers: In vitro degradation of poly(trimethylene carbonate), poly(trimethylene carbonate-co-caprolactone), and poly(adipic anhydride). *J. Appl. Polym. Sci.* **1995**, *57*, 87–103.
- (4) Wang, H.; Dong, J. H.; Qiu, K. Y. Synthesis and characterization of ABA type block copolymer of poly(trimethylene carbonate) with poly(ethylene glycol): Bioerodible copolymer. *J. Polym. Sci. Part A: Polym. Chem.* **2000**, *36*, 695–702.
- (5) Edlund, U.; A.-C. Albertsson,; S.K. Singh,; I. Fogelberg,; B.O. Lundgren, Sterilization, storage stability and in vivo biocompatibility of poly(trimethylene carbonate)/poly(adipic anhydride) blends. *Biomaterials* **2000**, *21*, 945–955.
- (6) Pêgo, A.; Luyn, M. V.; Brouwer, L.; van Wachem, P.; Poot, A.; Grijpma, D.; Feijen, J. In vivo behavior of poly(1,3-trimethylene carbonate) and copolymers of 1,3-trimethylene carbonate with D,L-lactide or caprolactone: Degradation and tissue response. *J. Biomed. Mater. Res.* **2003**, *67A*, 1044–1054.
- (7) Zhang, Y.; xi Zhuo, R. Synthesis and drug release behavior of poly (trimethylene carbonate)-poly (ethylene glycol)-poly (trimethylene carbonate) nanoparticles. *Biomaterials* **2005**, *26*, 2751–2760.
- (8) Zhang, Z.; Grijpma, D. W.; Feijen, J. Thermo-sensitive transition of monomethoxy poly(ethylene glycol)-block-poly(trimethylene carbonate) films to micellar-like nanoparticles. **2006**, *112*, 57–63.
- (9) J.E.M. Habraken, W.; Zhang, Z.; G.C. Wolke, J.; Grijpma, D. W.; G. Mikos, A.; Feijen, J.; A. Jansen, J. Introduction of enzymatically degradable poly(trimethylene car-

- bonate) microspheres into an injectable calcium phosphate cement. *Biomaterials* **2008**, *29*, 2464–2476.
- (10) Sanson, C.; Schatz, C.; Meins, J.-F. L.; Brûlet, A.; Soum, A.; Lecommandoux, S. Bio-compatible and Biodegradable Poly(trimethylene carbonate)-b-Poly(l-glutamic acid) Polymersomes: Size Control and Stability. *Langmuir* **2010**, *26*, 2751–2760.
- (11) Sanson, C.; Meins, J.-F. L.; Schatz, C.; Soum, A.; Lecommandoux, S. Temperature responsive poly(trimethylene carbonate)-block-poly(L-glutamic acid) copolymer: polymersomes fusion and fission. *Soft Matter* **2010**, *6*, 1722–1730.
- (12) Chapanian, R.; Amsden, B. Combined and sequential delivery of bioactive VEGF165 and HGF from poly (trimethylene carbonate) based photo-cross-linked elastomers. *Journal of Controlled Release* **2010**, *143*, 53–63.
- (13) Jiang, X.; Xin, H.; Gu, J.; Xu, X.; Xia, W.; Chen, S.; Xie, Y.; Chen, L.; Chen, Y.; Sha, X.; Fang, X. Solid tumor penetration by integrin-mediated pegylated poly(trimethylene carbonate) nanoparticles loaded with paclitaxel. *Biomaterials* **2013**, *34*, 1739–1746.
- (14) Jiang, X.; Xin, H.; Ren, Q.; Gu, J.; Zhu, L.; Du, F.; Feng, C.; Xie, Y.; Sha, X.; Fang, X. Nanoparticles of 2-deoxy-D-glucose functionalized poly(ethylene glycol)-copoly(trimethylene carbonate) for dual-targeted drug delivery in glioma treatment. *Biomaterials* **2014**, *35*, 518–529.
- (15) Fukushima, K. Poly(trimethylene carbonate)-based polymers engineered for biodegradable functional biomaterials. *Biomater. Sci.* **2016**, *4*, 9–24.
- (16) Schüller-Ravoo, S.; Feijen, J.; Grijpma, D. Flexible, elastic and tear-resistant networks prepared by photo-crosslinking poly(trimethylene carbonate) macromers. *Acta Biomaterialia* **2012**, *8*, 3576–3585.

- (17) van Bochove, B.; Hannink, G.; Buma, P.; Grijpma, D. Preparation of Designed Poly(trimethylene carbonate) Meniscus Implants by Stereolithography: Challenges in Stereolithography. *Macromolecular Bioscience* **2016**, *16*, 1853–1863.
- (18) Zant, E.; Grijpma, D. Tough biodegradable mixed-macromer networks and hydrogels by photo-crosslinking in solution. *Acta Biomaterialia* **2016**, *31*, 80–88.
- (19) van Bochove, B.; Schüller-Ravoo, S.; Grijpma, D. W. Photo-Crosslinked Elastomeric Bimodal Poly(trimethylene carbonate) Networks. *Macromolecular Materials and Engineering* **2019**, 1800623.
- (20) Geven, M.; Varjas, V.; Kamer, L.; Wang, X.; Peng, J.; Eglin, D.; Grijpma, D. Fabrication of patient specific composite orbital floor implants by stereolithography. *Polymers for Advanced Technologies* **2015**, *26*, 1433–1438.
- (21) Schüller-Ravoo, S.; Zant, E.; Feijen, J.; Grijpma, D. Preparation of a Designed Poly(trimethylene carbonate) Microvascular Network by Stereolithography. *Advanced Healthcare Materials* **2014**, *3*, 2004–2011.
- (22) Hallary, J.-L., Lauprêtre, F., Monnerie, L., Eds. *Polymer Materials, Macroscopic Properties and Molecular Interpretations*; John Wiley & Sons: Hoboken, 2010.
- (23) Tanzi, M. C., Farè, S., Eds. *Characterization of Polymeric Biomaterials*; Elsevier: Cambridge, 2017.
- (24) Prigogine, I., A., R. S., Eds. *Advances in Chemical Physics Vol. LXVI*; John Wiley & Sons: New York, 1987.
- (25) Laws, D. D.; Bitter, H.-M. L.; Jerschow, A. Solid-State NMR Spectroscopic Methods in Chemistry. *Angew. Chem. Int. Ed.* **2002**, *41*, 3096–3129.
- (26) Schmidt-Rohr, K., Spiess, H. W., Eds. *Multidimensional Solid-State NMR and Polymers*; Academic Press: London, 2005.

- (27) Webb, G. A., Ed. *Modern Magnetic Resonance*; Springer: Cham, 2006.
- (28) Carr, H. Y.; Purcell, E. M. Effects of Diffusion on Free Precession in Nuclear Magnetic Resonance Experiments. *Phys. Rev.* **1954**, *94*, 630–638.
- (29) Meiboom, S.; Gill, D. Modified SpinEcho Method for Measuring Nuclear Relaxation Times. *Review of Scientific Instruments* **1958**, *29*, 688–691.
- (30) Cohen-Addad, J. Effect of the anisotropic chain motion in molten polymers: The solid-like contribution of the nonzero average dipolar coupling to NMR signals. Theoretical description. *J. Chem. Phys.* **1974**, *60*, 2040–2053.
- (31) Cohen-Addad, J. P.; Schmit, C. Nuclear magnetic resonance approach to fractal chain structure in molten polymers and gels: Characterization method of the spin-system response. *Polymer* **1988**, *29*, 883–893.
- (32) Sotta, P.; Fülber, C.; Demco, D. E.; Blümich, B.; Spiess, H. W. Effect of Residual Dipolar Interactions on the NMR Relaxation in Cross-Linked Elastomers. *Macromolecules* **1996**, *29*, 6222–6230.
- (33) Sotta, P. Local Order and Induced Orientation in PDMS Model Networks, Studied by ^2H NMR. *Macromolecules* **1998**, *31*, 3872–3879.
- (34) Mellinger, F.; Wilhelm, M.; Belik, P.; Schwind, H.; Spiess, H. W. Quantitative determination of dynamic heterogeneities in coreshell latices by ^1H solid-state NMR. *Macromol. Chem. Phys.* **1999**, *200*, 2454–2460.
- (35) Fechete, R.; Demco, D.; Blümich, B.; Eliav, U.; Navon, G. Anisotropy of collagen fiber orientation in sheep tendon by ^1H double-quantum-filtered NMR signals. *J. Magn. Res.* **2003**, *162*, 166–175.
- (36) Saalwächter, K. ^1H multiple-quantum nuclear magnetic resonance investigations of

- molecular order in polymer networks. II. Intensity decay and restricted slow dynamics. *J. Chem. Phys.* **2004**, *120*, 454–464.
- (37) Saalwächter, K.; Kleinschmidt, F.; Sommer, J.-U. Swelling Heterogeneities in End-Linked Model Networks: A Combined Proton Multiple-Quantum NMR and Computer Simulation Study. *Macromolecules* **2004**, *37*, 8556–8568.
- (38) Yen, Y.-S.; Pines, A. Multiple-quantum NMR in solids. *J. Chem. Phys. Part II* **1983**, *78*, 3579–3582.
- (39) Baum, J.; Munowitz, M.; Garroway, A. N.; Pines, A. Multiplequantum dynamics in solid state NMR. *J. Chem. Phys.* **1985**, *83*, 2015–2025.
- (40) Baum, J.; Pines, A. NMR Studies of Clustering in Solids. *J. Am. Chem. Soc.* **1986**, *108*, 7447–7454.
- (41) Saalwächter, K.; Ziegler, P.; Spyckerelle, O.; Haidar, B.; Vidal, A.; Sommer, J. U. ^1H multiple-quantum nuclear magnetic resonance investigations of molecular order distributions in poly(dimethylsiloxane) networks: Evidence for a linear mixing law in bimodal systems. *J. Chem. Phys.* **2003**, *119*, 3468–3482.
- (42) Saalwächter, K.; Herrero, B.; López-Manchado, M. A. Chain Order and Cross-Link Density of Elastomers As Investigated by Proton Multiple-Quantum NMR. *Macromolecules* **2005**, *38*, 9650–9660.
- (43) Saalwächter, K. Proton multiple-quantum NMR for the study of chain dynamics and structural constraints in polymeric soft materials. *Prog. Nucl. Magn. Reson. Spectrosc.* **2007**, *51*, 1–35.
- (44) Chassé, W.; Schlögl, S.; Riess, G.; Saalwächter, K. Inhomogeneities and local chain stretching in partially swollen networks. *Soft Matter* **2013**, *9*, 6943–6954.

- (45) Mansilla, M.; Valentín, J.; López-Manchado, M.; González-Jiménez, A.; Marzocca, A. Effect of entanglements in the microstructure of cured NR/SBR blends prepared by solution and mixing in a two-roll mill. *E. Polym. J.* **2016**, *81*, 365–375.
- (46) Lorthioir, C.; Randriamahefa, S.; Deloche, B. Some aspects of the orientational order distribution of flexible chains in a diblock mesophase. *J. Chem. Phys.* **2013**, *139*, 224903.
- (47) Lorthioir, C.; Deloche, B. Heterogeneous behavior of free chain-ends in a lamellar diblock copolymer: segmental dynamics and ordering, as probed by ^2H solid-state NMR. *Colloid Polym. Sci.* **2014**, *292*, 1841–1851.
- (48) Saalwächter, K.; Heuer, A. Chain Dynamics in Elastomers As Investigated by Proton Multiple-Quantum NMR. *Macromolecules* **2006**, *39*, 3291–3301.
- (49) Chávez, F. V.; Saalwächter, K. Time-Domain NMR Observation of Entangled Polymer Dynamics: Analytical Theory of Signal Functions. *Macromolecules* **2011**, *44*, 1560–1569.
- (50) Martin-Gallego, M.; González-Jiménez, A.; Verdejo, R.; López-Manchado, M. A.; Valentín, J. L. Epoxy Resin Curing Reaction Studied by Proton Multiple-Quantum NMR. *J. Polym. Sci. Part B Polym. Phys.* **2015**, *53*, 1324–1332.
- (51) Gjersing, E.; Chinn, S.; Giuliani, J. R.; Herberg, J.; Maxwell, R. S.; Eastwood, E.; Bowen, D.; Stephens, T. Investigation of Network Heterogeneities in Filled, Trimodal, Highly Functional PDMS Networks by ^1H Multiple Quantum NMR. *Macromolecules* **2007**, *40*, 4953–4962.
- (52) Vieyres, A.; Pérez-Aparicio, R.; Albouy, P.-A.; Sanseau, O.; Saalwächter, K.; Long, D. R.; Sotta, P. Sulfur-Cured Natural Rubber Elastomer Networks: Correlating Cross-Link Density, Chain Orientation, and Mechanical Response by Combined Techniques. *Macromolecules* **2013**, *43*, 889–899.

- (53) Giuliani, J. R.; Gjersing, E. L.; Chinn, S. C.; Jones, T. V.; Wilson, T. S.; Alviso, C. T.; Herberg, J. L.; Pearson, M. A.; Maxwell, R. S. Thermal Degradation in a Trimodal Poly(dimethylsiloxane) Network Studied by ^1H Multiple Quantum NMR. *J. Phys. Chem. B* **2007**, *111*, 12977–12984.
- (54) Gabrielle, B.; Lorthioir, C.; Lauprêtre, F. Thermal Aging of Interfacial Polymer Chains in Ethylene-Propylene-Diene Terpolymer/Aluminum Hydroxide Composites: Solid-State NMR Study. *J. Phys. Chem. B* **2011**, *115*, 12392–12400.
- (55) Bower, A. F., Ed. *Applied Mechanics of Solids*; CRC Press: Boca Raton, 2009.
- (56) Pérez-Aparicio, R.; Vieyres, A.; Albouy, P.-A.; Sanseau, O.; Vanel, L.; Long, D. R.; Sotta, P. Reinforcement in Natural Rubber Elastomer Nanocomposites: Breakdown of Entropic Elasticity. *Macromolecules* **2013**, *46*, 8964–8972.
- (57) de Anda, A. R.; Fillot, L.-A.; Long, D.; Sotta, P. Influence of the amorphous phase molecular mobility on impact and tensile properties of polyamide 6,6. *J. Appl. Polym. Sci.* **2016**, *133*, 43457.
- (58) Flory, P. J., Ed. *Principles of Polymer Chemistry*; Cornell University Press: Ithaca and London, 1953.
- (59) James, H. M.; Guth, E. Statistical Thermodynamics of Rubber Elasticity. *J. Chem. Phys.* **1953**, *21*, 1039–1049.
- (60) Landau, L. D., Lifshitz, E. M., Eds. *Theory of Elasticity*; Pergamon Press: Oxford, 1970.
- (61) Treloar, L., Ed. *The Physics of Rubber Elasticity*; Clarendon Press: Oxford, 1975.
- (62) Flory, P. J. Theory of elasticity of polymer networks. The effect of local constraints on junctions. *J. Chem. Phys.* **1977**, *66*, 5720–5729.

- (63) Flory, P. J. Molecular theory of rubber elasticity. *Polymer* **1979**, *20*, 1317–1320.
- (64) Akagi, Y.; Gong, J. P.; il Chung, U.; Sakai, T. Statistical Thermodynamics of Rubber Elasticity. *Macromolecules* **2013**, *46*, 1035–1040.

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