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ARTICLE

Cross-Linking Control of PDMS Rubber at High Temperatures Using TEMPO Nitroxide

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ABSTRACT: A novel composition using 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO) and dicumyl peroxide (DCP) for scorch delay and control of the final network topology of polydimethylvinylmethylsiloxane (vinyl-PDMS) at high temperatures has been proposed. The evolution of linear viscoelasticity during cross-linking reaction was carried out on parallel plate geometry rheometer. The rubber was cross-linked with different ratios of [TEMPO]/[DCP] in order to control scorch time, which is defined as the time during which the PDMS rubber can be worked at a given temperature before cross-linking begins (i.e., the time at which the complex shear modulus suddenly increases). We showed that scorch delay increases according to the amount of TEMPO acting as an inhibitor. Nuclear magnetic resonance spectroscopy (^{1}H NMR) has been used to investigate the effect of TEMPO. This study reveals that the delayed action is the result of a TEMPO-grafted polymer action formed by reaction between TEMPO and polymer radicals. Furthermore, polymeric radicals are rapidly trapped by a grafting reaction before they are able to form cross-links. The cross-linking density (ν) and the number of junctions (μ) have been obtained from the phenomenological network model of Langley and Dossin and Graessley. In addition, a differential scanning calorimeter (DSC) was used to characterize the cross-linking reaction. Specific heat data show two exothermic reactions. These reactions may be associated on one hand to the decomposition of DCP and TEMPO grafting in vinyl-PDMS and on the other hand to the C−C covalent bonds creation. The DSC results indicate that the variation of scorch time with the [TEMPO]/[DCP] ratio is in reasonable agreement with those obtained from rheological measurements. Finally, an original method based on DSC experiments was derived to estimate the density of chemical junctions in PDMS networks. This method is based on the balance between the enthalpy of created cross-linked bonds and the standard enthalpy for one covalent carbon−carbon bond. Interestingly, predicted numbers of chemical junctions are in close agreement with those calculated using viscoelastic data.

1. Introduction

PDMS rubbers or silicone products maintain its mechanical and electrical properties over a wide range of temperatures.[1] They are used for the production of seals in the automotive and aerospace industry, implants and devices for medical purposes, and packaging in the food industry.[2] PDMS rubbers are made by cross-linking functionalized polydimethylsiloxane. Commonly, a major curing mechanism frequently used for PDMS is the generation of polymer radicals through the use of organic peroxides that subsequently combine to form carbon−carbon bonds.[3] This exothermic and irreversible chemical process converts a viscous entanglement of long-chain molecules of polymer into three-dimensional elastic network.[4] The most frequently used organic peroxides are dialkyl peroxides, such as dicumyl peroxide. Different mechanisms have been proposed to explain the cross-linking of the PDMS by dialkyl peroxides.[5] Dluzneski has proved the inability of alkoxy radicals to abstract hydrogen from a methyl of the PDMS for thermodynamic reasons.[6] Therefore, the presence of vinyl functional groups in the polymer chain enables the free-radical cross-linking of PDMS.[7] In this case, the generated peroxide radicals initiate cross-linking by addition to the double bonds.[8] With this curing mode stable carbon−carbon bonds are formed.[9]

Typically, peroxide-cured PDMS rubbers shows an increase in Young's modulus; the resulting cured rubber should have a good compression set and high processing temperature.[10] However, free-radical cross-linking by peroxide suffers from premature cross-linking at high temperatures, which is called scorching.[11] High temperatures lead to the partial decomposition of peroxide, thus inducing to the imperfections in the form (inhomogeneity) and roughness in the surface of the final product caused by gel particles in the body of the cross-linked product.[12] Thus, control of cross-linking reaction cannot be overemphasized. Delayed mechanisms and reactions kinetics have been discussed and reviewed in the literature.[13] In his patent, Robert[14] described a process for grafting a functional monomer, in particular maleic anhydride, onto a thermoplastic polymer in presence of a nitroxide such as TEMPO, the role of which is to avoid cross-linking during the grafting operation. It should be noted that nitroxides are mostly used like stable free radicals in the controlled radical polymerization.[15] Nitroxyl-mediated free radical polymerization (NMP) techniques are valued for their reported ability to prepare polymers with a narrow molecular weight distribution[16] and block copolymer structure.[17] Solomon et al.[18] demonstrate that at the low temperatures typically associated with standard free

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radical polymerizations (40−60 °C) TEMPO reacted at near diffusion-controlled rates with carbon-centered free radicals, generated from the addition of initiating radicals to vinyl monomers. The resulting alkoxyamine derivatives were essentially stable at these temperatures, thus acting as radical traps.

Recently, Chaudhary et al.[19] showed that the reaction of carbon-centered radicals with nitroxides and its derivatives can be a novel means for scorch time and cure control in peroxide cross-linking of polyethylene thermoplastics. Although, several solutions have been proposed in the literature to control scorching and cure process of thermoplastics. In contrast, control of free-radical cross-linking of rubber materials has never been discussed. Consequently, the molecular understanding of the network topology−cross-linking kinetics relationships still remains incompletely understood. This is primarily because conventional elastomers formed by random cross-linking methods have very obscure structure with a broad network strand length distribution and an unknown number of dangling chains.[20]

The ultimate objective of this work is to propose a novel way using of nitroxides to control free-radical cross-linking chemistry and topological parameters of final networks such as the length of the network strands, functionality of cross-links, the amounts of entanglements, and dangling chains. A complete investigation about the effect of TEMPO in this free-radical mechanism is described in this paper.

2. Experimental Materials and Procedures

PDMS. PDMS of high molecular weight (PDMS gum) from ABCR was used. The number-average ($\overline{M}_n = 300\,000$ g mol^{-1}) and weight-average ($\overline{M}_w = 650\,000$ g mol^{-1}) were determined by size exclusion chromatography (SEC). This PDMS contains 0.2 mol % of vinyl groups. The molar weight of molecular segment between two consecutive reactive sites, i.e., between two vinyl sites, is therefore $M_0 = 37\,000$ g mol^{-1}.

Free-Radical Cross-Linking. Dicumyl peroxide (DCP, M = 270 g mol^{-1}) was used as the free-radical initiator of the cross-linking reaction, and the nitroxide 2,2,6,6-tetramethylpiperidinyloxyl (TEMPO, M = 156 g mol^{-1}) was used as the scorch reactant. Both products were purchased from Aldrich and used without any further purification. All experiments were carried out with an identical concentration in DCP: [DCP] = 36 mol m^{-3}. The concentration of TEMPO was calculated in order to have the following molar ratios (r = [TEMPO]/[DCP]): r = 1.2, 1.6, 1.8, 2, and 2.4.

Rheological Measurements. The rheological experiments were carried out on a Rheometrics mechanical spectrometer (RMS800) using a parallel-plate geometry (R = 12.5 mm). The parallel plate system was preheated at the temperature of the experiment. Then, the sample was put between the plates once the temperature of regulation was reached. The rheological kinetics of cross-linking were carried out in real time at only one pulsation (ω = 1 rad s^{-1}) and at different temperatures T = 140, 160, 180, and 200 °C. At the end of this cross-linking process, a frequency sweep experiment ($10^{-2} < \omega$ (rad s^{-1}) $< 10^{2}$) was performed on the same sample at the same temperature to determine the equilibrium modulus ($G_e = \lim_{\omega\to 0} G'(\omega)$). In all experiments, sample response linearity with respect to strain amplitude was verified, and nitrogen gas was used to prevent thermal oxidation. In this type of experiment, we assumed that DCP and TEMPO were perfectly dispersed in molten polymer at a molecular scale (homogeneous conditions of reaction).

Network Characterization. The PDMS network was characterized by the soluble fraction (ω_s) only. Tetrahydrofuran (THF) was used as good solvent at room temperature. Specimens taken from the vulcanized sheet were immersed in THF for 72 h at 25 °C. Swollen samples at equilibrium were taken out from the solvent, blotted with filter paper, and weighed immediately. Samples were subsequently dried in a vacuum oven for 24 h at 70 °C and reweighed. The soluble fraction was then be directly measured.

Dynamic Scanning Calorimetry (DSC). Differential scanning calorimeter equipment manufactured by TA Instruments (Q100 system), equipped with sealed aluminum pans, was used to measure the heat of cross-linking reactions. The mass of the samples ranged from 20 to 23 mg. A sealed empty pan was used as a reference. The total heats of reactions were obtained from isothermal conditions (T = 160 °C) or nonisothermal method (heating rate: $\dot{T}$ = 2.5 °C min^{-1}). All experiments were performed under nitrogen purge.

NMR. As previously explained, samples with different molar ratio [TEMPO]/[DCP]) were prepared at 160 °C in a rheometer oven. First of all, un-cross-linked samples (i.e., samples totally soluble) cured up to the scorch time were characterized. The stability of the TEMPO-polymer graft was studied by analysis of the soluble fraction of cross-linked sample obtained at the end of the cross-linking reaction. All these samples were dissolved in chloroform ($CHCl_3$) for 24 h at 25 °C. ^{1}H NMR study was performed at room temperature. Spectra were obtained with an ALS Bruker 300 MHz spectrometer.

Thermogravimetry Coupled Gas Chromatography/Mass Spectroscopy (TGA-GC/MS). TGA coupled with gas chromatography−mass spectrometry (GC-MS) was performed with an Agilent 6890 series GC system equipped with an HP-5 ms (5% phenyl)methylpolysiloxane, ref 19091S-433. Injection and detection by MS were carried out at 200 °C. The degradation was measured from the TGA results.

3. Results and Discussion

3.1. Rheology. Cross-linking of vinyl-PDMS by organic peroxide is believed to be achieved via a free-radical mechanism, which involves three key steps as shown in Figure 1: (step 1) the generation of two cumyloxy radicals by thermal decomposition of the peroxide, (step 2) cumyloxyl radicals attack the unsaturated pendant groups (vinyls) in the polymer chain via addition reaction to generate polymer radicals, and (step 3) the polymer radicals produced are quite reactive, so that they can add to another polymer radicals to form a covalent carbon−carbon cross-link. As a result, the molecular chain mobility is strongly affected and the storage and loss moduli increase with time as shown in Figure 2 for T = 140 °C. At a particular point, the storage and loss moduli cross each other. It was shown [21] that the gel point of a cross-linking polymer coincides with the $G'-G''$ crossover only if the power law on both storage and loss moduli followed the power law $G' \propto G'' \propto \omega^n$ with n = 1/2. According to our previous results, it can be assumed in the present study that the crossover between $G'(t)$ and $G''(t)$ defines the gel point of a network based on polymer precursor of high molecular weight. In other words, we admit the storage and loss moduli are equal over the whole spectrum of frequencies and proportional to the square of the frequency. Reaching this critical point, named gel point, the PDMS chains form a three-dimensional network. Above the gel point, the density of the network increases and the storage modulus reaches a steady-state value ($G_e = 2.6 \times 10^5$ Pa) corresponding to the end of the cross-linking reaction. Interestingly, the loss modulus passes through a maximum (just above the gel point) and decreases to a constant value ($\tan\delta = G''/G' = 8.0 \times 10^{-3}$). A possible explanation of this behavior stands from the fact that, thanks to the cross-linking reaction, high molar masses polymers are first formed which results in increases of both the storage and loss moduli. However, beyond the gel point, the increase of the elasticity is the leading factor, and the network tends to be more and more perfect so that $\tan\delta$ decreases with higher density network to finally reach an equilibrium value.

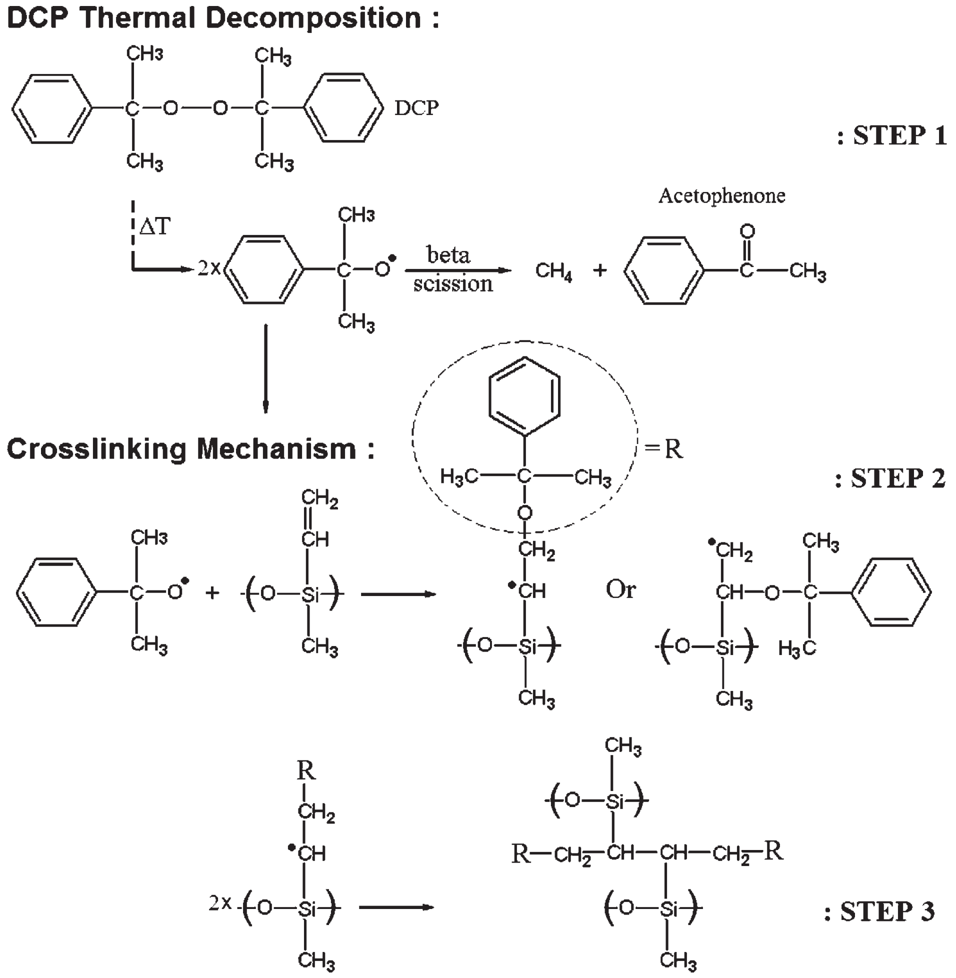

Figure 1. DCP decomposition and free-radical cross-linking mechanisms of vinyl-PDMS.

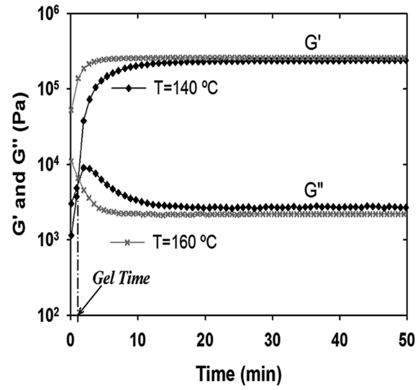

Figure 2. Radical cross-linking of vinyl-PDMS initiated by 36 mol m^{-3} of DCP. Variation of the storage G' and loss G'' modulus vs reaction time. T = 140 and 160 °C. ω = 1 rad s^{-1}.

At higher temperatures (T = 160 °C) the thermal decomposition of DCP is fast according to the high-energy activation of DCP decomposition ($E \approx 156$ kJ mol^{-1}). Therefore, the curves at these temperatures cannot capture the initial stage of cross-linking (gelation process) as one part of DCP is already decomposed during the preparation of the sample between the plates of the rheometer, estimated to be around 30 s. However, it can be qualitatively observed that the same cross-link density has been obtained after reaction completion. According to our previous works,[22] the present work shows that the efficiency of DCP does not depend on temperature, at least for temperature lower than 160 °C. Obviously, it is clear that the time needed by the modulus to reach a plateau gets longer as the temperature is lower (kinetic effect).

The influence of the TEMPO concentration, via the ratio r = [TEMPO]/[DCP], on scorch time and cross-linking density of PDMS network is shown in Figure 3a,b. From a qualitative point of view, Figure 3a (r = 1.8 for illustrative example) shows that the cross-linking process is delayed by few minutes. The scorch time is defined in Figure 3b as the time at which the storage modulus suddenly increases. At 160 °C, the addition of TEMPO results in an increase of the scorch time from 7.2 min (r = 1.2) to 16.9 min (r = 2.0). Surprisingly, the cross-linking reaction is totally inhibited at higher amount of TEMPO (r = 2.4). Although the scorch mechanism has been reported in the literature,[19,23] such quantitative experiments from TEMPO addition have been never shown in the literature.

According to a free radical cross-linking mechanism, it can be hypothesized that cross-linking delay is the result of a TEMPO-grafted polymer action formed by reaction between TEMPO and the polymer radical. Furthermore, polymeric radicals are rapidly trapped by a grafting reaction with TEMPO before they are able to form cross-links by combination. NMR techniques were employed to clarify chemical bond formation involved during PDMS cross-linking controlled by TEMPO. Figure 4 compares the NMR spectrum of virgin PDMS (Figure 4a) and reactive samples (Figure 4b,c). Reactive sample (Figure 4b) has been obtained

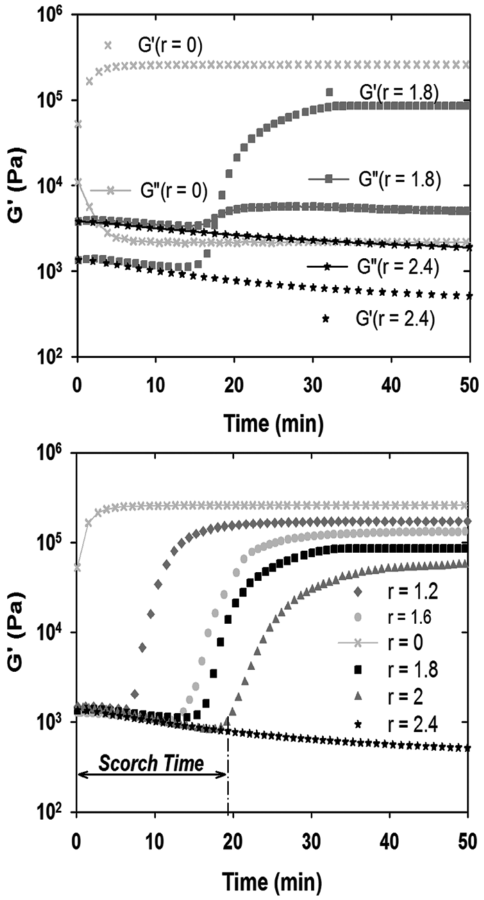

Figure 3. (a) Variation of the storage and loss modus at the following ratio: r = 0, 1.8, and 2.4. (b) Variation of the storage modulus (r = 0, 1.2, 1.6, 1.8, 2, and 2.4). Definition of the scorch time.

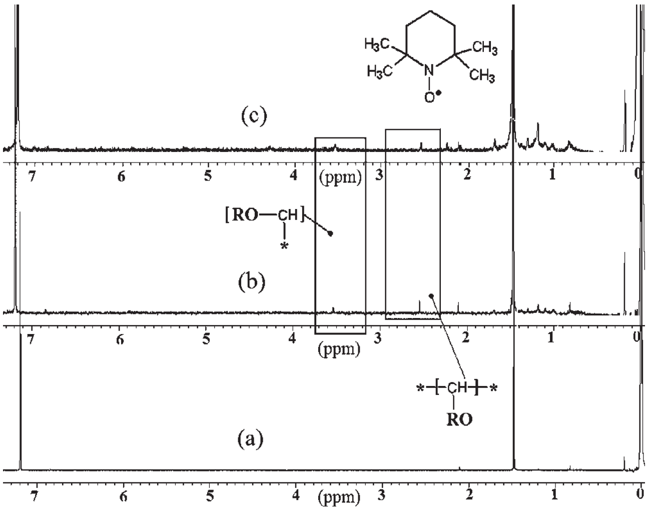

Figure 4. ^{1}H NMR spectrum proving TEMPO grafting onto PDMS (r = 1.8, T = 160 °C): (a) virgin vinyl-PDMS; (b) reactive vinyl-PDMS sample: curing time 15 min, the sample is totally soluble; (c) reactive vinyl-PDMS sample: curing time 30 min. The spectrum corresponds to the soluble fraction.

upon the following reactive conditions between the plates of the rheometer: $r = 1.8$, curing time = 15 min. From Figure 3a, b ($T = 160$ °C) this sample has not reached its gel point and is still soluble. Finally, Figure 4c shows the NMR spectrum of the soluble fraction of the same sample (r = 1.8) but cross-linked in a rheometer for 30 min. The ^{1}H spectrum of the virgin PDMS sample (Figure 4a) exhibits the expected signals at 7.2 ppm of the chloroform ($CHCl_3$) and 0 ppm of the tetramethylsilane (TMS). The chemical shifts at 0.2 and 0.8 ppm can be assigned to $Si-CH_3$ resonance. The strong peak at 1.5 ppm shows the presence of water residue in the sample. Moreover, a broad signal around 2.1 ppm can be observed and is attributed to CH groups. However, in the ^{1}H NMR spectra the peaks for the terminal ($-CH_2=CH$) double bond should be observed at 5.8 and 6.7 ppm;[24] the absence of this peak is due to the low molar concentration of vinyl groups in the PDMS sample. The comparison of the ^{1}H spectrum (Figure 4b,c) with the spectrum of the reference sample (Figure 4a) shows evidence of the TEMPO grafting onto the polymer chains. Additional resonances can be found in spectra b and c.

The primary indication for grafting in presence of TEMPO is the existence of new peaks at 2.55 and 3.55 ppm which are attributed to the formation of C$-$O bonds (i.e., $R-O-CH-$ and $R-O-CH_2$ species). However, the most significant modification is the presence of oxygen$-$carbon bonds formed by the addition of the cumyloxyl radicals after the peroxide decomposition. The ^{1}H spectrum (Figure 4b,c) shows the additional resonances in the range from 1 to 1.3 ppm which are typical of the CH_2 and CH_3 groups of TEMPO.[25] Therefore, the present ^{1}H NMR results prove the presence of TEMPO onto PDMS chains of reactive samples. Furthermore, these results indicate also the stability of bonds formed between the nitroxyl and carbon-centered radicals at elevated temperatures of processing.

From a quantitative point of view, the phenomenological model of Langley[26] and Dossin and Graessley,[27] which takes into account the contribution of chemical cross-links and trapped physical entanglements to prediction of the shear equilibrium modulus, can be used in the present study. According to the entanglement interpretation of the topological contributions, a portion of the restrictions on configurational rearrangements of macromolecules becomes permanently trapped when a chemical network is formed and therefore is able to contribute to the equilibrium elasticity.[28] The contributions to the modulus are given by the widely used Langley equation:

$$G_e^{\text{Langley-Graessley}} = G_{ch} + T_e G_N^0 \tag{1}$$

Here, the equilibrium modulus G_e is given as the sum of the modulus G_{ch} due to chemical cross-links and the trapped entanglement term ($T_e G_N^0$), where T_e (called the Langley trapping factor) is the proportion of the maximum concentration of topological interactions that contribute to the modulus, and G_N^0 is the plateau modulus related to the entangled molecular weight ($G_N^0 = \rho RT/M_e$). According to the arguments based on the constrained-junction model,[29] the term G_{ch} should equate to the phantom network modulus,[30] onto which contributions from entanglements are added:

$$G_{ch} = (\nu - h\mu)RT \tag{2}$$

where h is an empirical parameter between zero and one but genarally considered to be equal to 0. The parameters ν (density of strands elastically actives), μ (density of cross-link bonds), and T_e for the phenomenological model can be calculated using the theoretical relations established by Pearson and Graessley.[31,32] According to these equations, assuming a tetrafunctional network and from the measurement of the soluble fraction ω_s, the parameters ν, μ, and T_e

Table 1. Kinetics and Linear Viscoelastic Parameters of PDMS Networks Cross-Linked at 160 °C in the Presence of Different Concentrations of TEMPO[a]

[TEMPO] (mol m^{-3})	r = ([TEMPO]/[DCP])	scorch time (min)	gel time (min)	G_e (Pa)	tan(δ)
0	0			2.6×10^5	0.008
43	1.2	7.2	8.2	1.7×10^5	0.012
58	1.6	13	15.6	1.3×10^5	0.024
65	1.8	14.1	17.7	8.6×10^4	0.057
72	2	16.9	21.9	5.9×10^4	0.1

[a] Initial concentration in DCP:[DCP] = 36 mol m^{-3}.

Table 2. Topological Parameters for the Different Samples, As Computed from the Theoretical Relations Derived by Pearson and Graessley[32]

r	ω_s	p	T_e	ν (mol m^{-3})	μ (mol m^{-3})	G_e (Pa)
0	0.018	0.83	0.58	18.3	10.1	2.3×10^5
1.2	0.04	0.513	0.43	10	5.6	1.6×10^5
1.6	0.06	0.4	0.34	6.9	4	1.2×10^5
1.8	0.095	0.3	0.24	4.3	2.6	8.5×10^4
2	0.14	0.231	0.16	2.7	1.6	5.6×10^4

have been calculated (see Table 2) for the different [TEMPO]/[DCP] ratios. Furthermore, the conversion p of vinyl groups consumed by the reaction of cross-linking can also calculated by this method. The rubbery modulus G_N^0 of entangled PDMS chains has been reported in the literature by Plazek et al.[33] and Valles and Macosko[34] to be 2.0×10^5 Pa at room temperature. Assuming an entropic elasticity of G_N^0, we finally calculated $G_N^0 = 2.9 \times 10^5$ Pa at $T = 160$ °C. Finally, the comparison of G_e experimental (Table 1) with G_e computed (Table 2) shows very satisfactory agreement which validates our approach based on the Pearson and Graessley model.

First of all, Table 1 ($r = 0$, $T = 160$ °C) shows that the conversion of vinyl groups belonging to the network is close to 83%. Therefore, the DCP efficiency is low for the cross-linking reaction as it is about 31% (DCP efficiency = $(0.83 \times 27)/(36 \times 2)$, where 27 is the molar concentration of vinyl function (expressed in mol m^{-3}), 36 is the molar concentration of DCP which gives two radicals when reacting, and 0.83 is the conversion of vinyl groups). However, this DCP efficiency is in good agreement with the literature results. For example, Hulse et al.[35] prove that the overall cross-linking efficiency for LPE with DCP is between 20 and 40% (at 150 °C) of the theoretically expected value. Moreover, it has been proved that cross-linking of high-consistency silicone rubbers such as vinyl-PDMS using peroxide leads to formation of peroxide's volatile residues such as acetophenone.[9] These breakdown products explain the low efficiency of DCP. Therefore, we obtained about 62% cumyloxyle and 38% methyl reactive ($CH_3^\bullet$) radicals after DCP decomposition. On the other hand, Table 1 shows that in presence of TEMPO the optimal ratio (r) necessary to cross-link the vinyl-PDMS is between 2 and 2.4. Consequently, the TEMPO efficiency is about 21% at $T = 160$ °C. This was unsurprising result because TEMPO could be involved in coupling reaction with $CH_3^\bullet$ radicals, leading to the formation of methyl-TEMPO.[25] Indeed, the grafting reaction was comparatively slow, presumably because the diffusion of polymer radicals is constrained.

Nevertheless, methyl-TEMPO formation is not the only side reaction for the present system. Figure 3b shows a slowly decreasing of the storage modulus at the earlier stage of reaction. This phenomenon is clearly shown for $r = 2$ and 2.4, and from our rheological investigations it results from polymer chain degradation. Furthermore, this side reaction was studied by TGA-GC/MS experiments. As a result, Figure 5 shows the mass spectra of vinyl-PDMS containing 1 wt % of TEMPO and cured for 30 min at the temperature $T = 200$ °C. This analysis proves the formation of major degradation products of PDMS such as the cyclic volatile oligomer decamethylcyclopentasiloxane (D5) and the ion fragment trimethylsiloxane (M_3T).[36,37] Indeed, in the presence of trace of water and metal in polymer, nitroxides can oxidize the reduced form of metal trace from the syntheses process of the polymer, while they themselves are reduced to hydroxylamines[38] as shown in Figure 6. Therefore, the change of nitroxide to a strong base due to the presence of water and catalyst residues in polymer leads to silanolate formation and depolymerization of the PDMS chains. This depolymerization mechanism has been already studied in the literature. Thomas[39] and Grassie and Macfarlane[40] described that cleavage of the PDMS backbone by moisture and contamination by strong bases or acids is the principal mode of depolymerization at lower temperatures 120−275 °C and is of most concern in normal operating environments.

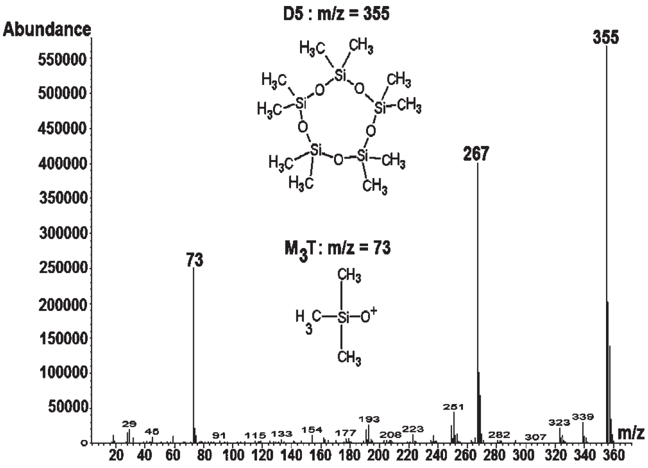

Figure 5. Overlay mass spectra of vinyl-PDMS with 1% of TEMPO at 200 °C.

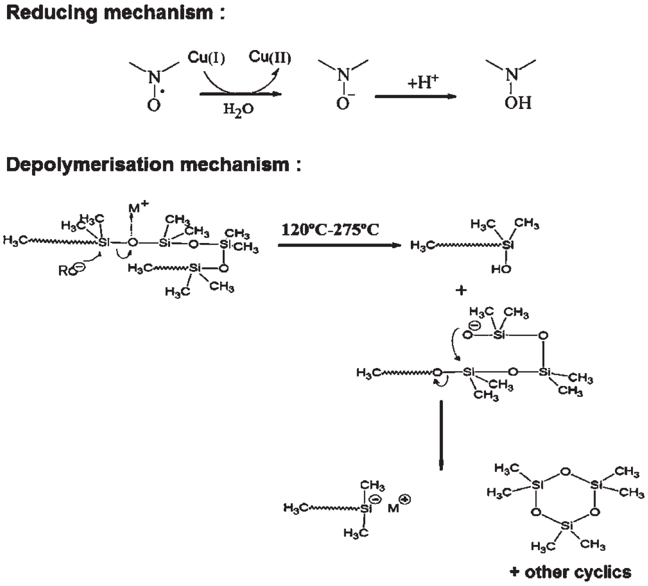

Figure 6. Proposed mechanisms for reduction of TEMPO and depolymerization of PDMS.[38−40]

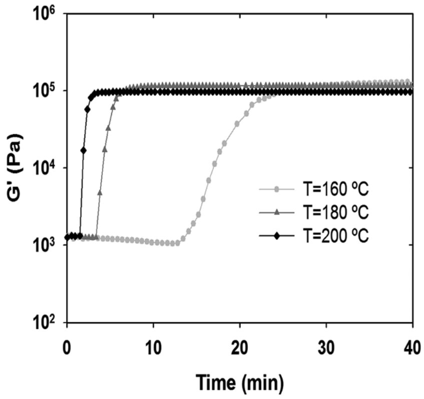

Figure 7. Temperature dependence (T = 160, 180, and 200 °C) of the cross-linking reaction: Variation of the storage modulus vs time for r = [TEMPO]/[DCP] = 1.6.

Finally, Figure 7 (r = 1.6) shows that the steady-state value of the complex shear modulus does not seem to depend on the temperature (T = 160, 180, and 200 °C), which is a balance between increase of both the modulus (entropic elasticity) and the defects with temperature. Then, temperature can be considered to have not effect in the stability of the nitroxyls graft and thus on the final cross-linking degree. In fact, the thermal stability of bonds formed between the nitroxyl and carbon-centered radicals has been studied extensively in model systems.[41] The results presented in these studies indicate that primary and secondary alkoxyamines should be robust enough to withstand processing and testing conditions at elevated temperatures for many hours to several days or longer, such that the integrity of grafts to primary and secondary carbons will be maintained. However, it can be noted that scorch delay decreased with increasing of temperature. The scorch time shifted from 13 min at 160 °C to 3.4 min at 180 °C and to 1.5 min at 200 °C. This is unsurprising results because the kinetics of TEMPO grafting and chains combination increase with temperature. However from these results, the activation energy of each process cannot be achieved.

DSC Analysis. The cross-linking reaction consists to create covalent bonds between the macromolecular chains of polymer. These covalent bonds are obtained by reaction between reactive sites, and they are formed with releases a quantum of energy, making cross-linking an exothermic reaction. We propose hereafter to use the differential scanning calorimetry to investigate the PDMS cross-linking controlled by the addition of TEMPO. This technique is expected to study the cross-linking process at the molecular scale and to relate the variation of the cross-linked bonds formed between the macromolecular chains in presence of TEMPO with the change of the physical properties of final networks.

The isothermal DSC scans of (PDMS/DCP/TEMPO) curing system at different amount of TEMPO (r = 0, 1.2, 1.4, 1.6, 2, and 2.4) are shown in Figure 8. Interestingly, these DSC kinetics allowed us to separate the own exothermic heat of C−C bonds creation (or quantum of energy of formed cross-linked bonds) in a complex system of the other reactions like the homolytic decomposition of the initiator (DCP) and its addition on the polymer chains. Actually, as shown in Figure 8, the addition of TEMPO in the PDMS/DCP system results in a secondary exothermic peak. This second peak is time shifted with increasing the TEMPO concentration. Eventually at r = 2.4, this second peak disappears. These DSC results show the complexity of the present system as two exothermic phenomena with different apparent enthalpies have been revealed. These two phenomena can associated to two different reactions. In the absence of TEMPO, the global reaction is related to DCP decomposition, vinyl sites activation, and C−C bonds creation (Figure 1).

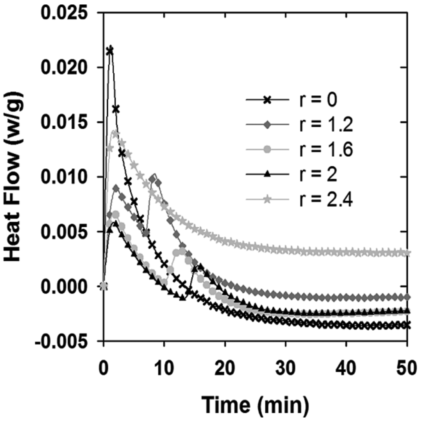

Figure 8. DSC traces showing the total heat of cross-linking reaction obtained for various r = [TEMPO]/[DCP] ratio at 160 °C.

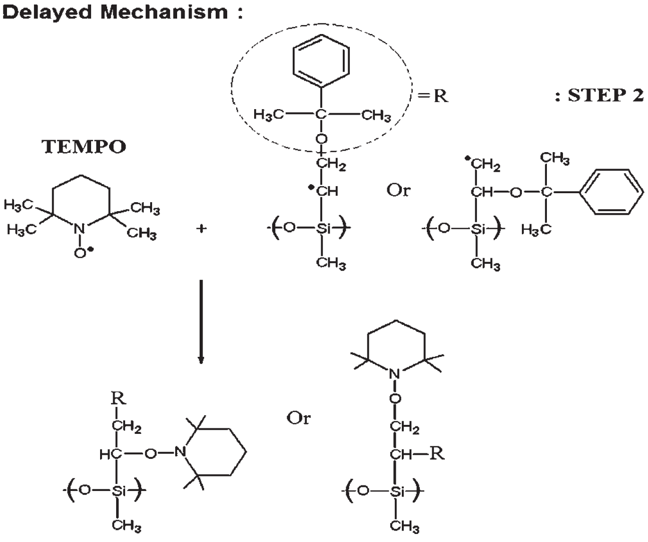

Figure 9. Mechanism for delayed-action (scorch time) of TEMPO on free-radical cross-linking of vinyl-PDMS.

However, in the presence of TEMPO, the first exothermic peak corresponds to DCP decomposition, vinyl sites activation, and the grafting of nitroxyl radicals on the polymeric radicals as shown in Figure 9. This last mechanism prevents the formation of cross-link bonds. Once all TEMPO molecules are consumed, the second peak can then arise. This peak is then assigned to the C−C bonds creation. This hypothesis was validated by the fact that this second peak disappears with increasing the TEMPO concentration above a critical value ($r > 2$) at which the cross-linking reaction is not observed anymore. Moreover, these results are in perfect agreement with rheology results. Indeed, time corresponding to the second peak (t_{picR2} from Table 3) for the various samples coincides well with the scorch time determined by rheology (Table 2). A small difference is observed between DSC and rheological data due to the temperature control between the two techniques.

More precisely, the rheology and DSC results for r = 1.2 are compared in Figure 10. Both techniques are quite

Table 3. DSC Results at 160 °C and Predicted Density of Chemical Junctions Using the DSC Method

r	t_{R2} (min)	t_{peakR2} (min)	ΔH_{C-C} (J g^{-1})	μ (mol m^{-3})
0				8.4[a]
1.2	7.1	8.4	1.71	4.8
1.6	10	12.6	1.26	3.6
2	13.4	15.7	0.87	2.5

[a] From extrapolation of data at r = 1.2, 1.6, and 2.

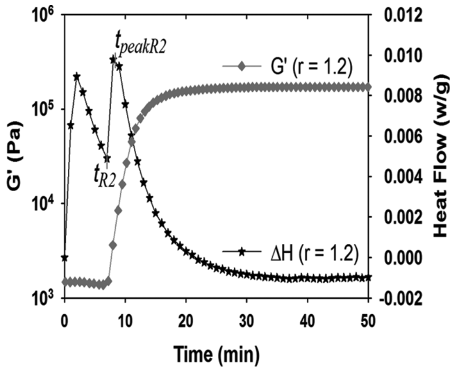

Figure 10. Comparison of the variation storage modulus and enthalpy of the reaction (r = 1.2, T = 160 °C).

complementary for the kinetic study of this complex reactive system. At the earlier stages of the reaction, the rheology does not record any variation of the viscoelastic properties since TEMPO react with polymer radical and then embed the cross-linking reaction. On the contrary, DSC analysis shows a first exothermic peak of reaction which is spread out until the starting time (scorch time) of the complex modulus variation. This result confirms our last hypothesis: the first phase corresponds to the DCP decomposition, vinyl sites activation, and the addition of nitroxyl radicals on the polymeric radicals (DSC exothermic peak and no variation of the complex shear modulus). The end of this inhibition phase is announced by both techniques: strong variation of the complex shear modulus and evidence of a second exothermic peak. Therefore, this second peak corresponds to the network formation through to the covalent bonds formation (or chemical cross-link) between the PDMS polymer chains.

Generally speaking, DSC experiments in both isothermal and anisothermal modes have mostly used in the literature to study the kinetics of cure reactions.[42] Several alternative methods for estimating the cross-linking density with DSC has been discussed in the literature for thermosets like the epoxy−amine systems. However, in the case of elastomer cross-linking there is no a significant variation of the heat capacity during the reaction. Furthermore, the methods generally used are based on the assumption that the rate of heat generation is proportional to the rate of the cure reactions.[43] This is questionable for a complex reaction system. In their work on the kinetic of vulcanization of a natural rubber compound, Ding and Leonov[44] described that DSC data were found to be incompatible with the cure meter test because the complex vulcanization reaction system is multiexothermal. Therefore, DSC analysis was never used to calculate the extent of the cross-linking reaction in terms of cross-linking density.

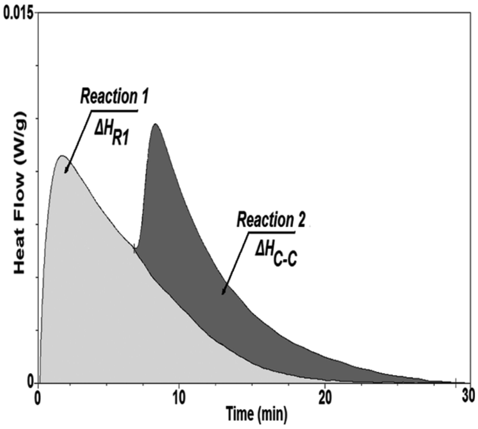

Figure 11. Principle of the experimental method to calculate the enthalpy ΔH_{C-C} of cross-link C−C bonds. r = 1.2, T = 160 °C.

In the present work, it is assumed that the enthalpy of C−C covalent bonds (ΔH_{C-C}) can be separated from the other reactions and derived from the total enthalpy ΔH_T as follows:

$$\Delta H_{C-C} = \Delta H_T - \Delta H_{R1} \tag{3}$$

where ΔH_{R1} is the enthalpy of the first reaction including DCP decomposition, vinyl sites activation, and grafting of nitroxyl radicals on the polymer chains. Therefore, the chemical cross-link density can be calculated according to the following equation:

$$\mu = \frac{\rho_{polymer} \Delta H_{C-C}}{\Delta H^0_{C-C}} \tag{4}$$

where ΔH^0_{C-C} is the standard enthalpy to form one mole of C−C bonds. According to the literature,[45] ΔH^0_{C-C} = 347 kJ mol^{-1}.

Experimentally, the enthalpy (ΔH_{C-C}) was derived as shown in Figure 11, and the cross-linking density was calculated according to eq 4. These values are reported in Table 3. It should be noted that the cross-linking density for r = 0 (TEMPO free) has been calculated by a linear extrapolation of the values obtained for r = 1.2, 1.6, and 2. According to Tables 2 and 3, chemical cross-link densities calculated from soluble fraction (Langley and Dossin and Graessley model) and DSC analysis are in good agreement even if the latter underestimated the cross-linking density.

From using the same extrapolation, the total amount of TEMPO necessary to totally inhibit the cross-linking reaction is then equal to 102 mol m^{-3}. Translating this value in terms of [TEMPO]/[DCP] ratio leads to r = 2.8. This result is in agreement with the value observed from rheological measurement r = 2.4, for which no cross-linking reaction was observed.

4. Conclusion

The roles of nitroxides such as TEMPO in scorch delay and cross-linking control of free-radicals cross-linking process have been demonstrated in this study. A remarkably scorch delay has been found with varying the molar ratio [TEMPO]/[DCP] in the range r = 0−2.4. First of all, rheological measurements were carried out in order to determine the linear viscoelastic properties of the PDMS networks. The scorch and gel times, the equilibrium modulus (G_e), and the soluble PDMS chains fraction were found to be a function of the concentration of TEMPO. Furthermore, the characterization of the network features based on the phenomenological model of Langley and Dossin and Graessley provided that the control of the network topology can be achieved by using nitroxide TEMPO. In agreement with rheological measurements, NMR microstructural studies revealed that the cross-linking delayed action in the presence of TEMPO is the result of trapped carbon-centered polymer radicals by nitroxides. As a result, once the TEMPO is totally consumed, the cross-linking can proceed as usual.

Furthermore, DSC was used to characterize the effect of TEMPO in cross-linking reaction at the molecular scale. An original result has been shown using this technique by varying the molar ratio [TEMPO]/[DCP]. Correlation between DSC and rheometry experiments proved that the secondary exothermic enthalpy corresponds to the covalent bonds formation between only carbon-centered polymer radicals and thus the network formation. According to this result, we developed an original method to determine the chemical cross-link density in the case of complex cure reaction system which has multiexothermal heat reaction. The predicted chemical cross-link densities are in close agreement with those calculated using the phenomenological model of the viscoelasticity.

Finally, the findings of this study will be an important impact in polymer science from both an academic and an industrial viewpoint. This interest is governed by the need to control the network architecture in order to develop new class of elastomer formulations with a rich variety of topological characteristics improved and/or new mechanical and physical properties.

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