

Photooxidation of polyoctenamer: viscoelastic assessment of gel formation

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Abstract

The evolution of viscoelastic properties upon photoageing of polyoctenamer has been monitored using dynamic oscillatory experiments with the aim of comparing with the more usual data obtained by conventional techniques such as FTIR spectroscopy. Our finding is that the average molecular weight increased from the start of the UV exposure, involving rapid cross-linking. At the gel point, a power law frequency dependence of the dynamic storage modulus ($G' \propto \omega^{n'}$) and loss modulus ($G'' \propto \omega^{n''}$) was observed with $n' = n'' = n = 0.4$. Moreover, the gel time was accurately determined, $t_{\text{gel}} = 160$ min. Whereas, at the same time, no chemical change was detected by FTIR spectroscopy. Hence, compared to conventional chemical analysis, dynamic rheological measurements consist of an additional method. Its sensitivity for the determination of the molecular structure evolution through photoageing of elastomeric materials has been clearly illustrated. In addition, melt rheology results are in good agreement with the dual processes of photochemical evolution of polyoctenamer previously described from conventional results. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Photooxidation; Elastomer; Gel point

1. Introduction

Elastomeric materials are especially sensitive to oxidative degradation. Numerous studies of thermo-oxidation, photooxidation and ozonolysis of such materials have been published and attempts to predict their long-term behavior have been reported [1–12]. However, it is worthwhile to note that most lifetime data are related to chemical changes detected during the degradation process. Relationships between these chemical changes and the physical properties evolution of the material are generally not well known [13,14].

Recent investigations suggested that cross-linking largely controls photooxidation of elastomers [8,9,15,16]. During photoageing, a decreasing oxygen permeability coefficient has been observed with the extent of sample degradation, which has been associated with cross-linking and presumably causes the oxidation to become limited in the later stages of degradation [3,8,9,15,17]. A previous study [18] reported on the identification of the chemical structure of the three-dimensional network by using ^{13}C nuclear magnetic resonance (NMR). New resonances of carbon atoms

involved in cross-linking have been detected in the aliphatic region, but any mechanism could not be clearly elucidated. Thus, we decided to focus our attention on the changes in molecular parameters through photoageing in order to accurately determine the gel point. Indeed, the gel point of a cross-linked polymer is an important parameter, both from scientific and technological standpoints. For instance, with the view to recycle polymer wastes, it is necessary to know when the gelation occurs as the polymer can be easily processed only before the gel point while it can still flow and the stresses applied can relax to zero [19]. Accurate knowledge of the gel point would also allow estimation of the efficiency of stabilizing systems. Hence, stabilizers have to prevent any evolution of both chemical and molecular structure of the material. Antioxidants inhibit the formation of oxidative groups (carbonylated and hydroxylated species), but it is necessary to check that they also inhibit the physical evolution of the polymer (cross-linking, chain scission...).

It is well known that the evolution of the rheological material properties directly reflects changes in molecular parameters. Thus, melt rheology provides a convenient tool to view the particular behavior of a gelling system from the liquid state to the solid state. The linear viscoelastic properties in dynamic experiments are sensitive to the

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three-dimensional network formation and can be used to precisely determine the gel point [20–23].

Then, in the present study, we report on the use of melt rheology applied to polyoctenamer photoageing with the aim of comparing with the more usual results obtained by conventional techniques as FTIR spectroscopy (including derivatization reactions [24,25], specific chemical analysis [26,27] and physical treatments), previously published [28].

2. Background

Gelation is the phenomenon by which a cross-linked polymeric material undergoes a phase transition from the liquid to the solid state at a critical point of time, temperature, concentration, etc. Hence, the sol–gel transition, known as the gel point, occurs at some critical extent of the cross-linking reaction [19].

Winter and Chambon proposed a general criterion that can be used to identify the gel point. They have shown that at the gel point, both the elastic modulus (G') and the viscous modulus (G'') exhibit a power-law dependence on the frequency of oscillation ω [29–32]. The corresponding expressions describing dynamic moduli at the gel point are as follows:

$$G'(\omega) = S\Gamma(1 - n) \cos(n\pi/2)\omega^n \quad (1)$$

$$G''(\omega) = S\Gamma(1 - n) \sin(n\pi/2)\omega^n. \quad (2)$$

The relaxation exponent n can have values in the range of $0 < n < 1$, in agreement with previous works of the literature on various model networks.

Thus, at the gel point, the storage and viscous moduli depend on frequency in an identical manner, corresponding to parallel lines in a frequency spectrum:

$$G'(\omega) \propto G''(\omega) \propto \omega^n. \quad (3)$$

In addition, from Eqs. (1) and (2), the loss tangent $\tan \delta$ becomes independent of frequency (ω), but proportional to the relaxation exponent n :

$$\tan \delta = G''/G' = \tan(n\pi/2). \quad (4)$$

Then, the frequency independence of the loss tangent in the vicinity of the gel point has been widely used to determine the gel point of cross-linked polymers [21–23,33].

3. Experimental section

3.1. Sample preparation

The polymer used is polyoctenamer rubber named Vestenamer[®] 8012, produced by Hüls. This compound is a low-molecular-weight polymer with a broad molecular weight distribution, made from cyclooctene by metathesis polymerization. It consists of linear as well as cyclic macromolecules which are unbranched and contain one double

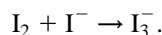
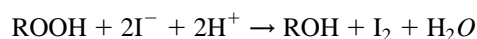
bond per eight carbon atoms with 80% of the double bonds arranged in a *trans* configuration (based on NMR determination). It was precipitated twice from chloroform solution into methanol to remove possible additives. Films (about 100 μm) were prepared by compression molding between two polyester sheets at 60°C under 100 bar for 1 min.

3.2. Photooxidation procedure

Films were fixed on aluminium holders and then irradiated in a polychromatic set up. A “medium pressure” mercury source filtered by borosilicate envelope (Mazda type MA 400) supplies radiation of wavelengths longer than 300 nm. This source is located along the focal axis of a cylinder with elliptical base. Sample films turned around the other focal axis. The inside of the chamber is made of highly reflectant aluminium. Temperature of the samples is controlled by a thermocouple connected with a temperature regulator device, which controls a fan. All the experiments were carried out at 35°C. Films were analyzed after various exposure times.

3.3. Analysis

Chemical changes were detected by FTIR spectroscopy (Nicolet Impact 400, Omnic[®] software). Total peroxides were estimated by iodometric titration [26,27] based on the reduction of hydroperoxides by sodium iodide in excess in acidic medium according to the reaction:



The concentration of the triiodide subsequently formed is measured by UV spectrophotometry at 362 nm using the commonly accepted extinction coefficient of $2.5 \times 10^4 \text{ mol}^{-1}/\text{l} \cdot \text{cm}^{-1}$. Size Exclusion Chromatography (SEC) measurements in THF at room temperature gave the following molecular characteristics: $M_w = 107\,400 \text{ g/mol}$, $M_n = 50\,100 \text{ g/mol}$ and $M_w/M_n = 2.1$. Narrow polystyrenes were used as standards for calibration of SEC.

3.4. Rheological experiments

The changes in dynamic storage G' and loss G'' moduli of photooxidized Vestenamer[®] were followed in oscillatory shear mode using a rotational controlled stress rheometer (StressTech/Rheologica) equipped with a parallel plates geometry. The plates diameter was 20 mm and the gap between the plates was about 1 mm. In all the cases, the values of the stress amplitude were checked to ensure that all measurements were conducted within the linear viscoelastic region. At different time during the UV exposure, a frequency sweep extending from 0.01 to 30 Hz was performed. Different temperatures have been tested, but the low value of activation energy involves a small

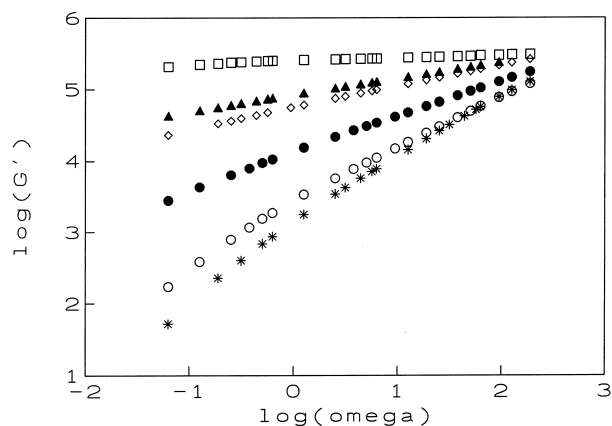


Fig. 1. Storage modulus G' as a function of frequency pulsation ($\omega = 2\pi N$) plotted at different UV exposure times for Vestenamer[®] films: (*) 0 h, (O) 1 h, (●) 2 h, (◇) 3 h, (▲) 5 h and (□) 10 h.

extension of the frequency range. Hence, all the experiments were carried out at 90°C. The stability of oxidized samples at 90°C with respect to the measurement duration has obviously been verified.

4. Results

4.1. Dynamic viscoelastic properties through photooxidation

The evolution of the storage G' and loss moduli G'' through photooxidation of Vestenamer[®] are illustrated in Figs. 1 and 2.

First, G' is always smaller than G'' , and both moduli vanish at low frequencies (terminal zone, $G' \propto \omega^2$, $G'' \propto \omega$). Hence, the frequency dependence curves show a liquid-like behavior. Then, the shapes of $G'(\omega)$ and $G''(\omega)$ change over the course of irradiation. At around 3 h of UV

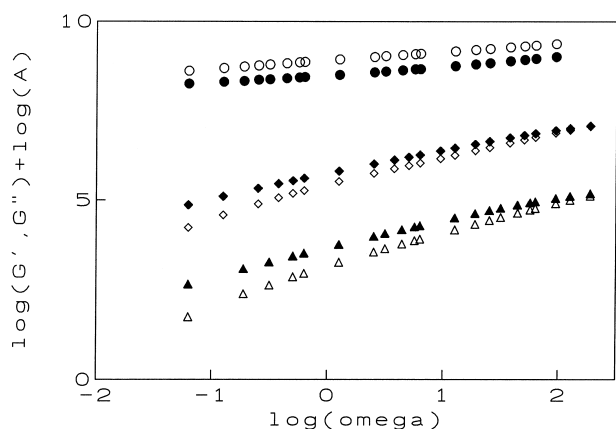


Fig. 2. Storage (G') and loss (G'') moduli as a function of frequency ω plotted at different UV exposure times for Vestenamer[®] films. The curves have been shifted vertically by a factor ($\log A$) for more convenient comparison. Open symbols correspond to G' and solid symbols to G'' ; (Δ , \blacktriangle) 0 h, (\diamond , \blacklozenge) 3 h ($\log A = 2$) and (\circ , \bullet) 10 h ($\log A = 4$).

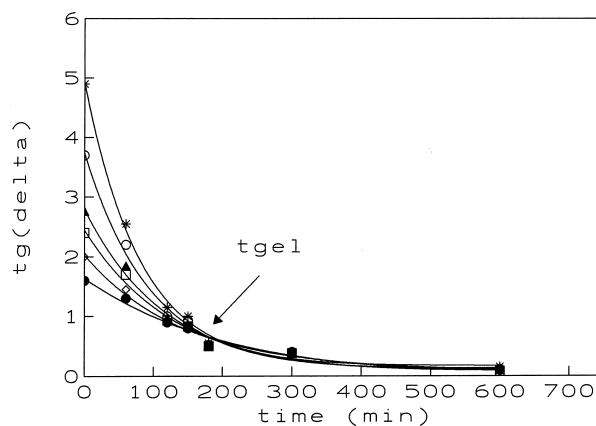


Fig. 3. Loss tangent, $\tan \delta$, as a function of UV exposure time for different frequencies: (*) 0.04 Hz, (□) 0.1 Hz, (▲) 0.4 Hz, (□) 1 Hz, (◇) 5 Hz and (●) 10 Hz. The notion t_{gel} marks the gel point.

exposure, G' and G'' look like parallel and show a power-law variation with respect to the frequency of oscillation (G' , $G'' \propto \omega^n$), indicating that the system is in the vicinity of the gel point. As photoageing proceeds, G' increases rapidly and becomes larger than G'' , which is a characteristic feature of the cross-linked system. The modulus of the fully cross-linked samples ($t > 10$ h) G' appears frequency independent.

Dynamic viscoelastic properties through photooxidation suggest that gelation of polyoctenamer occurs for around 3 h of irradiation time. Hence, we examine two methods for an accurate determination of the gel time (t_{gel}) for the gelling system obtained from oxidized Vestenamer[®].

4.2. Determination of the gel point

At the gel point, G' and G'' exhibit a power-law behavior with a common exponent, n . This definition of the sol–gel transition implies that $\tan \delta$ (gelation variable) loses its dependency on frequency and converges at the gel point. Fig. 3 depicts a multifrequency plot of $\tan \delta$ versus

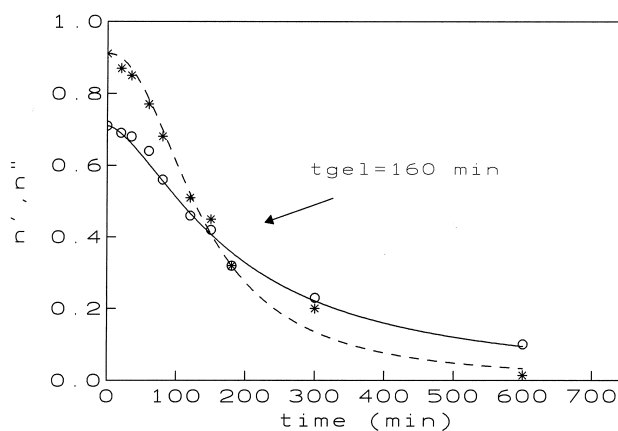


Fig. 4. Changes of apparent exponents n' (*) for storage and n'' (O) for loss moduli through irradiation of Vestenamer[®] films. The notion t_{gel} marks the gel point.

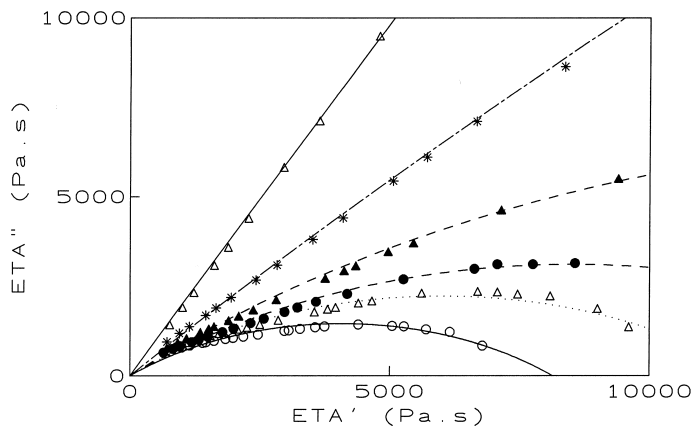


Fig. 5. Changes of complex viscosity components (η' , η'') through photooxidation of Vestenamer[®] using the Cole–cole representation; (η'' versus η') for different irradiation times: (○) 0, (△, dotted line) 20, (●) 60, (▲) 80, (*) 120 and (△, solid line) 180 min.

irradiation time of Vestenamer[®]. The values of $\tan \delta$ converge at a time corresponding to the gel time, t_{gel} . The value of t_{gel} is located in the approximate range 150–170 min. Then, the relaxation exponent n , simply calculated from the value of $\tan \delta$ at the gel time using Eq. (2), is close to 0.4.

An alternative way to determine gel points is by plotting the “apparent” viscoelastic exponents n' and n'' ($G' \propto \omega^{n'}$, $G'' \propto \omega^{n''}$), obtained from the approximate scaling laws of the frequency dependence of $G'(\omega)$ and $G''(\omega)$ versus irradiation time. Hence, curves become congruent and the crossover at $n' = n'' = n$ is an indicator of the gel point [21,33,34].

The values of apparent viscoelastic exponents for both G' and G'' decrease over the course of irradiation and intersect at an irradiation time $t_{\text{gel}} = 160$ min (see Fig. 4). The critical exponent, $n' = n'' = n$, equals 0.4.

These results are consistent with those previously determined by using the frequency independence of loss tangent δ . However, we prefer the second method to determine the gel point because of its accuracy to estimate the gel time, t_{gel} .

A number of studies have showed that n is not universal and varies with the gelling system. Relatively high values of n are observed for the physical (reversible) gels (“weak” gels), n is predicted to be between 2/3 and 1 [32], while the power law exponent values for chemical (irreversible) gels are covering almost the entire possible range ($0 < n < 1$) [21,23,29–31,35,36]. The relaxation exponent n depends on structural and connectivity properties of the incipient gel. A low n value implies that the material is a mostly elastic body with the limit of $G'' = 0$ at $n = 0$ [36].

Therefore, the molecular weight of the initial polymer is assumed to be an important parameter for the gel behavior. Therefore, several authors have investigated the effect of prepolymer molecular weight on the viscoelasticity of the critical gels [35,36]. They reported that n decreases with increase of prepolymer molecular weight for several systems. For instance, Izuka and Winter [36] showed that exponent of polycaprolactone critical gels varies from 0.91 to 0.31 as the number-average molecular weight of the initial polymer increases from 10^3 to 2×10^4 g/mol. The critical exponent of short molecules ($M_n < 10^4$ g/mol) is reported to decrease from about 0.9 to 0.5, while for long

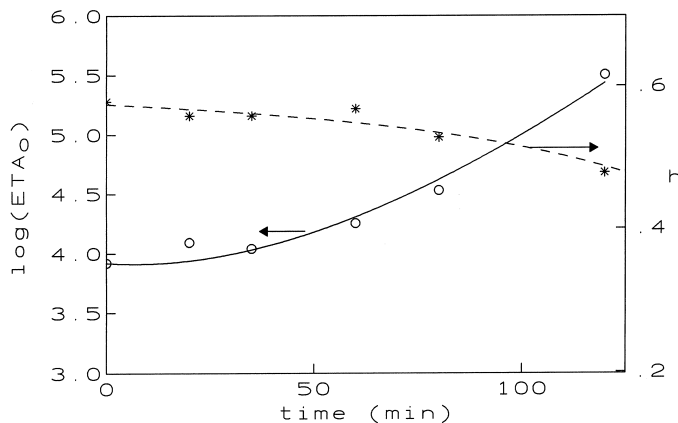


Fig. 6. Cole–cole parameters as a function of irradiation time for Vestenamer[®] in the pregel state: (○) zero shear viscosity η_0 , (*) relaxation-time distribution parameter h .

Table 1
Cole–cole distribution parameters through photoageing of Vestenamer®

Time (min)	η_0 (Pa. s)	h
0	8300	0.58
20	11 400	0.56
35	12 000	0.56
60	18 000	0.57
80	34 300	0.53
120	320 000	0.48
180	∞	–

molecules ($M_n > 10^4$ g/mol) n decreases from 0.5 to 0.3. Hence, we observe the same magnitude for our experimental exponent n with regards to this range of molecular weight, although our value was determined using polystyrene standards.

4.3. Evolution of molecular weight in the pregel regime

The average molecular weight increases as the cross-linking reaction proceeds, and diverges at the gel point [22]. This property could be used to measure the evolution of an incipient gel near the sol–gel transition. It is well known that the zero shear viscosity η_0 depends on the molecular weight and obeys to a power law [19]:

$$\eta_0 \propto M_w^\infty$$

Thus, at the gel point, the zero shear viscosity becomes infinite and immeasurable.

The zero shear viscosity η_0 can be obtained from the complex viscosity $\eta^*(\omega)$:

$$\eta^* = G^*(\omega)i\omega = \eta' - i\eta'' \quad \text{and}$$

$$|\eta^*|_{\omega \rightarrow 0} = |\eta'|_{\omega \rightarrow 0} = \eta_0.$$

An empirical rheological model used to fit dynamic data

is the Cole–cole distribution expressed by [37–39]:

$$\eta^*(\omega) = \eta_0/[1 + (i\omega\lambda_0)^{1-h}]$$

where λ_0 is the average relaxation time and h the parameter of the relaxation-time distribution.

In the complex plane this model predicts the variation of the viscosity components (η'' versus η') to be an arc of circle. From this representation it is easy to determine the parameters of the distribution: η_0 is obtained through the extrapolation of the arc of the circle on the real axis and the distribution parameter h through the measurement of the angle $\Phi = h\pi/2$ between the real axis and the radius going from the origin of the axis to the center of the arc of the circle.

Fig. 5 displays the evolution of the complex viscosity components through the photooxidation of Vestenamer®. In the pregel state, the zero shear viscosity η_0 rapidly increases (see Fig. 6), and then curves (η'' versus η') become straight lines in the vicinity of the gel point ($t_{\text{gel}} = 160$ min).

The initial high value of the distribution parameter ($h = 0.58$) is realistic with regards to the broad molecular weight distribution of the polyoctenamer sample ($M_w/M_n = 2.1$) [40] implying that viscoelastic exponents in the terminal zone ($n' = 0.9$ and $n'' = 0.7$) are far from the theoretical values (in the terminal zone: $n' = 2$, $n'' = 1$) in our experimental frequency range.

Moreover, as shown in Table 1, mass-average molecular weight drastically increases in the pregel regime (from the increase of η_0) without any evolution of the molecular weight distribution (h is quite constant up to the gel point). Hence, we assume that each macromolecular chain is equally involved in the photocross-linking process.

5. Discussion

In a previous article, the photochemical evolution of Vestenamer® has been reported [28]. The major

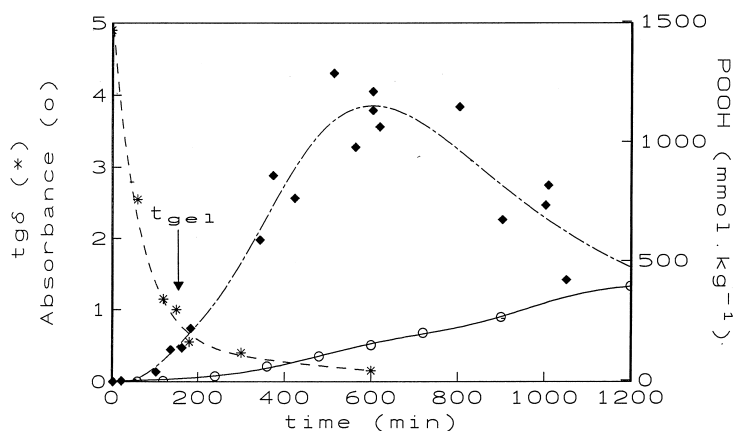


Fig. 7. Changes upon photooxidation of Vestenamer® films (100 μm). (○) FTIR data: kinetic curve of carbonylated photoproducts (Absorbance at 1715 cm^{-1}); (◆) hydroperoxides by iodometric titration; (*) Dynamic viscoelastic data: $\tan \delta$ as a function of UV exposure, the experimental frequency of oscillation is 0.04 Hz. The notion t_{gel} marks the gel point.

photoproducts resulting from oxidation have been identified and quantified using conventional techniques (FTIR spectroscopy including derivation reactions [24,25], specific chemical analysis [26,27] and physical treatments). Fig. 7 plots both the total hydroperoxides level as a function of exposure time and the kinetic curve of the formation of carbonylated photoproducts. At the earliest stage of photoageing, no chemical change is detected by FTIR spectroscopy ($t < 4$ h), while iodometric titration gives a significant content of hydroperoxides rising to a maximum at about 10 h, indicating an evolution of the chemical structure from the beginning of irradiation.

Likewise, dynamic oscillatory measurements underline an evolution of the molecular structure of the material from the start of the UV exposure. The drastic increase of η_0 in the pregel regime (see Table 1) provides evidence that molecular weight rapidly increases as photooxidation proceeds, involving cross-linking. Thus, in agreement with ROOH titration, no induction period exists.

Moreover, the characterization of the incipient gel leads to the accurate determination of the gel point, $t_{\text{gel}} = 160$ min of irradiation. The storage modulus G' increases by more than three orders of magnitude over the low frequency range during the first 5 h of UV exposure. Consequently, the material is considered fully cross-linked when photoproducts are detected by FTIR (at $t = 4$ –5 h). See Fig. 7.

Furthermore, 10 h of irradiation consists of a critical point. It is pointed out that the maximum in ROOH content observed for 10 h of photoageing in Fig. 7 corresponds with the inflexion point of the kinetic curve. Then, from conventional results, photooxidation of Vestenamer[®] is reported to exhibit dual processes [28]. In the first stage ($t < 10$ h), photooxidation reactions involve the formation of hydroperoxides, which are highly photounstable and rapidly undergo photolysis. In the second stage ($t > 10$ h), a photolytic process becomes predominant: photooxidation products undergo photolysis reactions (i.e. without oxygen). It is worthwhile to note that before 10 h of UV exposure, dynamic rheological experiments provide evidence of the drastic changes in the molecular structure of the material implying cross-linking. However, after 10 h, the storage modulus (G') appears frequency independent and tends towards an equilibrium value showing that the material is strongly cross-linked. Thereby, $\tan \delta$ becomes invariant with the irradiation time, as shown in Fig. 7. These observations indicate that the cross-linking density of the network increases only in a small extent after 10 h of photoageing. Thus, our experimental results are in good agreement with the previous proposal which assert that the photoageing of polyoctenamer involves two successive steps.

6. Conclusion

Comparing with the conventional techniques, dynamic oscillatory measurements give additional information

concerning molecular structure evolution involving cross-linking. Indeed, chemical analysis cannot reveal the network formation by cross-linking, however, it consists of a convenient method to identify subsequent photoproducts. We assume that melt rheology is a powerful tool (easy, accurate and very sensitive method) to monitor the molecular structure evolution of material through ageing. It provides an accurate diagnosis about gelation phenomenon, cross-linking extent and critical gel characterization. Hence, gelation occurs at the very beginning of photooxidation, and, the material is considered fully cross-linked when the photoproducts are detected by FTIR.

Acknowledgements

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