

Qualitative evaluation of the end-to-end correlation vector and of the mean square displacement of the molecules' center in a telechelic polymer under several shear rates values

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ABSTRACT

We present the results of molecular dynamics (MD) simulations of bead and spring models of associating polymers at melt-like densities. We consider telechelic polymers of general formula $AB_{12}A$ at different values of shear rate. The A atoms have self-associate properties, and this fact conducts to the construction of clusters or micelles that are interconnected by a number of bridging chains. This results in a physical gel that, depending on the interaction strength, can be weak and a reversible network, strong, or very strong. The corresponding micelles assume different forms too. Whenever a shear deformation is applied, two changes are observed: the clusters are broken and the chains stretch themselves (in a manner similar to a nematic liquid crystal) ordering in a different way from what is seen in bulk condition. In this paper we study for different A-A interactions and shear rate values the time's dependence of both the end-to-end correlation vector and the mean square displacement of the molecules' center.

Keywords: *associating polymers; gels; shear rate; molecular dynamics.*

1. INTRODUCTION

A telechelic polymer, probably the simplest example of an associating polymer, is a special type of linear heteropolymer that bears two groups capable of strong nonbonded interactions at its ends [1]. In turn, associating polymers comprises an important class within the much broader field of self-organizing soft materials or structured fluids (block copolymers, high- and low-molecular-weight liquid crystals, and lyotropic and amphiphilic systems) [2–7]. The association may be induced by several types of physical interaction: hydrogen bonding, a hydrophobic interaction between alkyl or aromatic groups [8], an association of perfluorated chains [9], electrostatic forces (ionomers) [7–10], complex formation, or supramolecular adducts [11, 12].

The most important physical and chemical properties of these polymers, which also form the basis for a wide range of applications, ultimately derive from associations of the terminal groups to form clusters, micelles, aggregates, or multiplets.

These polymers have been the focus of a sizeable number of theoretical studies [13–21] and computer simulations [22–33]. The precise structures of the aggregates and the behavior of the polymers under bulk conditions (for instance when they are confined to a narrow volume between two parallel surfaces [30] or to an isotropic volume [31]) have been clarified. Each terminal “bead” (i.e., terminal monomer or atom, also simply denoted “A”, whereas a non-terminal monomer or atom is denoted “B”) of such a polymer has self-associative properties, and tends to aggregate with other terminal beads, both in the same chain or different ones,

thus forming clusters, in bulk conditions. Depending on the interaction strength, these clusters may be reversible or not, may have medium or large dimensions and different forms. For high interactions the clusters are large and the corresponding packing of A atoms is regular, as in a solid (hexagonal or bcc) [31], resulting in a strong gel. In one of our previous works [32], we studied the consequences of applying a shear deformation to the physical structure: when a shear has applied, as expected, the clusters broke apart due to the destruction of every interaction between the A atoms. Otherwise, the most important result of this was that high deformation caused the chains to stretch, leading to an order similar to that seen in a nematic liquid crystal and forming new clusters between atoms from different chains.

In addition, in the last one [33] we studied the rheological behavior of the polymers and observed that the transformation of the morphological structure, equivalent to a double phase transition, conducted to a non-monotonous behavior of the stress deformation and an apparent negative viscosity.

In the present work we study the general dynamic behavior of the telechelic polymers under different values of shear and A-A interactions, presenting the correlation function for end-to end correlation vector (cvec) and mean square displacement of the center of molecules (msd) on time and indicative values for the correlation parameters.

2. MODEL AND COMPUTATIONAL METHOD

All simulations were carried out, as in our previous works [31–33], with the coarse-grained molecular dynamics code

COGNAC [34], but using the 8.3 more recent version. We adopted a standard coarse bead-and-spring representation of a generic

flexible polymer [35]. All chains in a given system were identical and had the generic formula $AB_{12}A$, where A is a terminal bead and B is an internal bead. In particular, the difference between the A and B monomers was represented by the energetic parameter ϵ_{ij} . We always took $\epsilon_{BB} = 1$, while the strength of the A...A interaction was allowed to vary, assuming four different values for ϵ_{AA} : 1 (corresponding to A = B and thus to weak homopolymer interactions), 4 (moderately strong interactions), 6 (strong interactions) and 7 (very strong interactions). At last, A...B interactions were evaluated, for every condition, as geometrical average between ϵ_{AA} and ϵ_{BB} according to the Lorentz–Berthelot combination rule [36]. Simulations were performed in the NVT ensemble, i.e., the number of chains N (no chemical reaction), the volume V, and the temperature T were all held constant.

3. RESULTS SECTION

Every simulation is a sequence of static configurations, each of them corresponding to a save. The difference between two consecutive savings corresponds to a time expressed in reduced units of $1000 \cdot 0.01$ being the integration time, τ , equal to 0.01. Studying a dynamic behavior the value corresponding to a time in the x axis is calculated as the average of all the possible differences of time. For example 100 is an average of all the couples of configurations whose difference is 100 while 12500 corresponds only to the difference between initial and final configurations, in a standard 1.25×10^6 time steps simulation. This fact conducts to have a more accurate statistics in a short-time range.

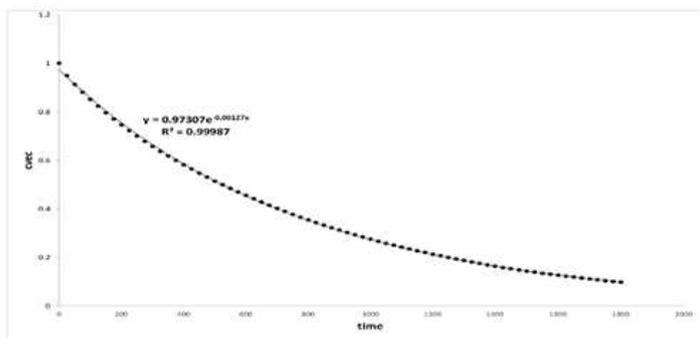


Figure 1a. Cvec depending on time for a homopolymer in bulk (standard simulation).

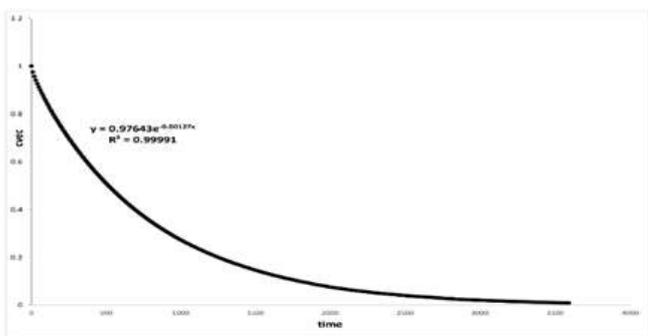


Figure 1b. Cvec depending on time for a homopolymer in bulk condition (long simulation).

For the homopolymer in bulk condition the Rouse

We considered seven different values of the shear rate γ (units: τ^{-1}): 0 (no shear); 5×10^{-5} (very low shear), 1×10^{-4} (low shear), 5×10^{-4} (average shear), 1×10^{-3} (quite high shear), 5×10^{-3} (high shear) and 1×10^{-2} (very high shear). We considered all possible interactions and shear values for a total of 28 different conditions. For every of them we performed new simulations, that required long equilibration stages, due to the new COGNAC version, starting from the homopolymer ($\epsilon_{AA} = 1$) in bulk condition ($\gamma = 0$). Following, we increased at first the A-A interactions, step by step, to 4, 6 7, and then, in a second time, the shear rate value for all the conditions. Finally, we obtained 2 different kinds of simulation: a standard 1.25×10^6 time steps, saving every 2,500, and a long one 10^7 time steps, saving every 1,000.

dynamics predicts an exponential ungrouping from 1 to 0 for the correlation vector[37], meanwhile the Einstein law applied to the Brownian motion indicates that the mean square displacement should be proportional to the time with a coefficient of $6D$, being D the diffusion coefficient[38].

First of all, we report in Figure 1a/b the correlation vector (cvec) and in Figure 2a/b the mean square displacement (msd), both depending on the difference of time. The figures labeled with a show the result of the 1.25×10^6 time steps simulations and the b labeled ones those of the 10^7 time steps calculations.

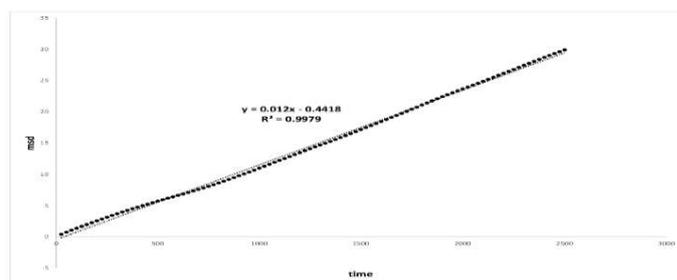


Figure 2a. Msd depending on time for a homopolymer in bulk (standard simulation).

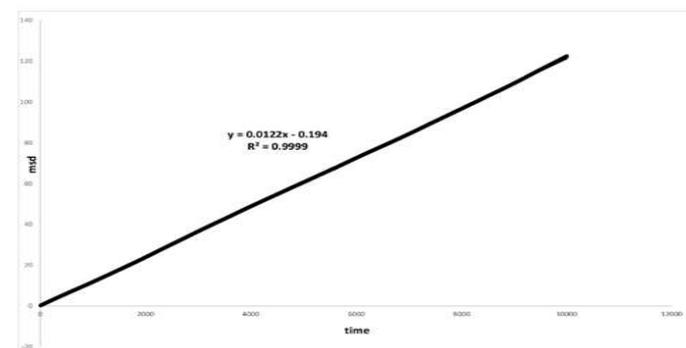


Figure 2b. Msd depending on time for a homopolymer in bulk (long simulation).

We can observe that there is a good agreement with the corresponding theory, both for the cvec and for the msd, but not perfect, so we decided to investigate better.

About $cvec$ it is possible to perform a simple mathematical operation that transforms the relation $cvec = \exp(-t/\tau)$ to $-\ln(cvec) = t/\tau$ which presents a linear correlation between the time and the $[-\ln(cvec)]$ quantity. If we build up the corresponding graphic (Figure 3a) we can see that an almost perfect line is shown except for a range at very short times. Considering only this part (Figure 3b) we can fit this last range exactly as a power law which corresponds to a stretched exponential in the original formula. In fact if the relation is $[-\ln(cvec)] = \alpha \cdot t^\beta$ the original expression becomes $cvec = \exp(-\alpha \cdot t^\beta)$, that is $cvec = \exp(-t/\tau)^\beta$. If we consider the other part of the curve (Figure 3c), the result is a linear correlation.

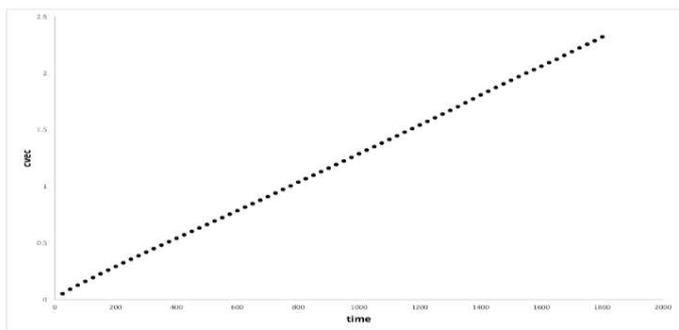


Figure 3a. $-\ln(cvec)$ quantity depending on time for a homopolymer ($\epsilon_{AA} = 1$) in bulk.

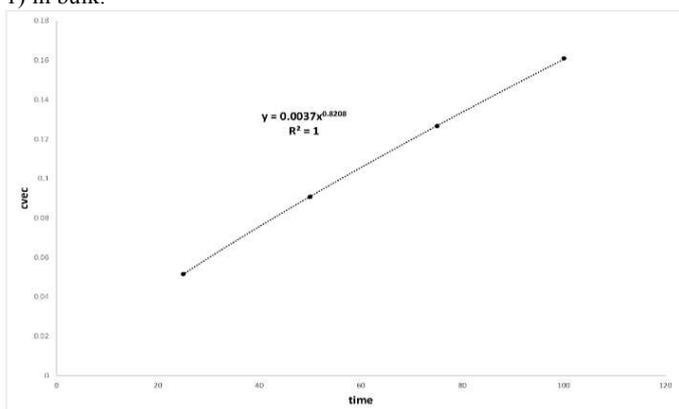


Figure 3b. Behavior of $-\ln(cvec)$ quantity at short times for a homopolymer in bulk (the result is a power law correlation vs time).

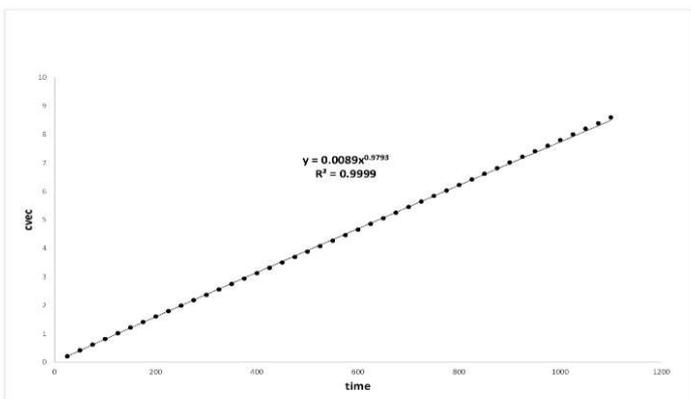


Figure 3c. Behavior of $-\ln(cvec)$ quantity, excluding short times, for a homopolymer in bulk (the result is a quasi-linear correlation vs time).

We point out a critical time, and a corresponding $cvec$ value, where the transition from the stretched exponential to the simple exponential occurs.

Now, we come back to the original relation and reduce the values in the following manner: the time corresponding to the

transition from stretched exponential to simple exponential becomes 0 and the following ones become real time minus transition time (in reduced units), meanwhile all the $cvec$ of this range are divided by the transition $cvec$ value.

The fit shown in Figure 4 confirms an exponential ungrowth, so that we can say that the behavior of a telechelic polymer, in bulk condition, is the same predicted from the Rouse theory except for very short times when the exponential ungrowth is stretched.

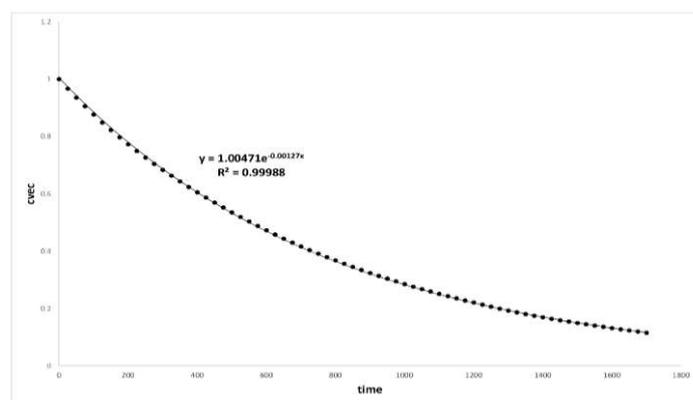


Figure 4. $cvec$ rescaled depending on time for a homopolymer in bulk.

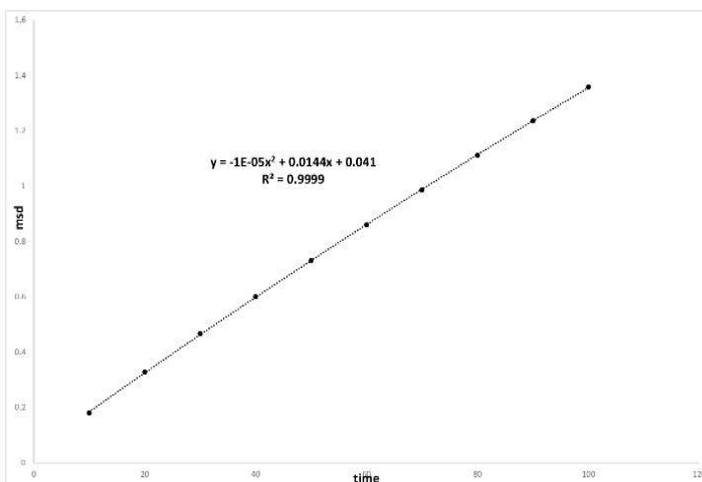


Figure 5a. Behavior of msd at short times for a homopolymer in bulk.

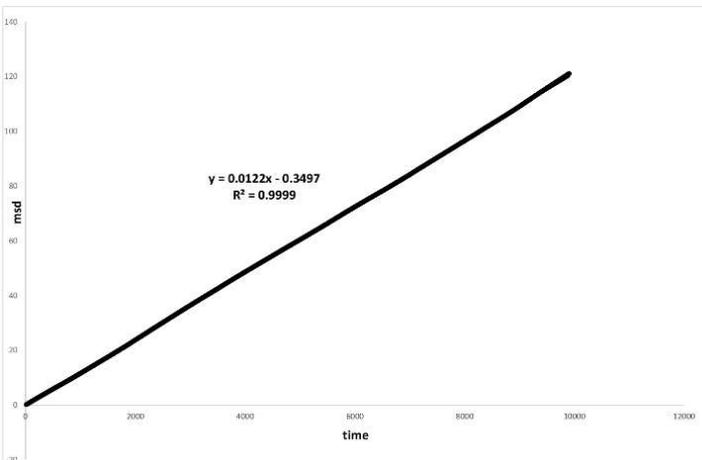


Figure 5b. msd rescaled depending on time for a homopolymer in bulk.

About msd it is necessary to observe the real values to understand that, similarly to $cvec$, the behavior differs from the predicted one for a very short time. In table 1 we point out in the first column the time values, in the second one the corresponding msd , and in the last the difference between the msd of the same

line and the previous one. Clearly if the correlation should be linear the differences should be the same. It is quite difficult to analyze the behavior of the polymer in the first range and we can simply try to obtain an empirical fit finding a quadratic one shown in Figure 5a. Exactly, as done for *cvec* we can rescale the values considering only the times subsequent to the transition, and confirm a linear correlation, in Figure 5b.

Table 1. The differences between two close values of *msd* reveal a non-linear correlation at short times.

time	msd	difference
10	0.179587	0.179587
20	0.327576	0.147989
30	0.466287	0.138711
40	0.600115	0.133828
50	0.731284	0.131169
60	0.859396	0.128112
70	0.985815	0.126419
80	1.111008	0.125193
90	1.235225	0.124218
100	1.358344	0.123118
110	1.480287	0.121944
120	1.602105	0.121818
130	1.72364	0.121535
140	1.844903	0.121263
150	1.966484	0.121582
160	2.087842	0.121357
170	2.209567	0.121726
180	2.330961	0.121394
190	2.451448	0.120487
200	2.572072	0.120625

The first part, reported in Figure 5a, will be investigated better in a forthcoming paper after having obtained more precise quantitative data.

Now we will examine the effects separately on *cvec* and *msd* from both increasing the A-A interaction and increasing the shear rate applied.

In Figure 6 we compare, in bulk conditions, the *cvec* for the four different A-A interactions (1, 4, 6, 7). In one of our previous papers [33] we showed that increasing them the polymer assumes the form of a weak gel, a strong gel and a very strong gel. Stronger is the gel, longer is the relaxing time of *cvec* and it is interesting to observe that the difference increasing from 1 to 4 is not so wide, meanwhile the increasing to 6 is more significant and the $\epsilon_{AA} = 7$ case is similar (but not equal) to the 6 one.

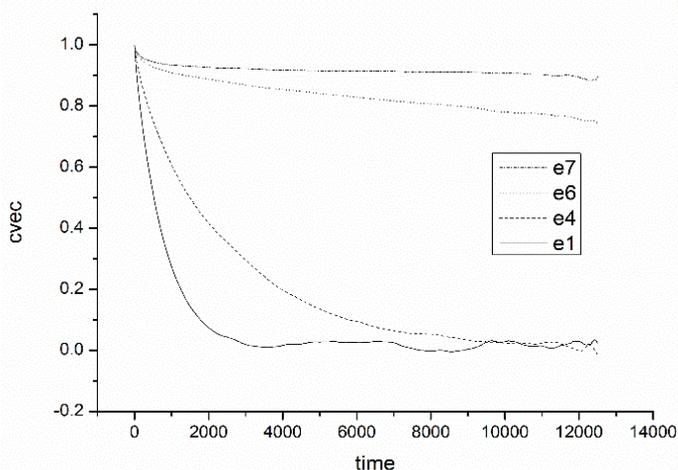


Figure 6. Influence of A-A interactions to the correlation between *cvec* and time in bulk conditions.

For the cases having A-A interactions 4, 6 and 7 values we use the same transformation explained for the homopolymer condition. The obtained result is that when the interactions are average the behavior is similar to the lower ones. We observed a power-law correlation, corresponding to the ungrouping stretched exponential in the original one, for short times, from zero to a critical time, and a linear correlation, corresponding to an ungrouping exponential in the first, for longer times. The unique difference is the transition time which is higher than for the $\epsilon_{AA} = 1$ condition.

When the interactions were high we obtained two important differences respect to the previous conditions: a unique power-law correlation for all the considered range shows a good but not perfect agreement, (Figure 7a), while a more accurate study reveals after a designed time the usual transformation to a linear one (Figure 7b). After a second critical time there is another linear correlation with different parameters (Figure 7c). The second observed result is a non-isotropic behavior along the three Cartesian directions: in Table 2 we show the values of all the *cvec* components in time range 4000-4500. The presence of cylindrical large clusters formed by A atoms [31] induces both these changes.

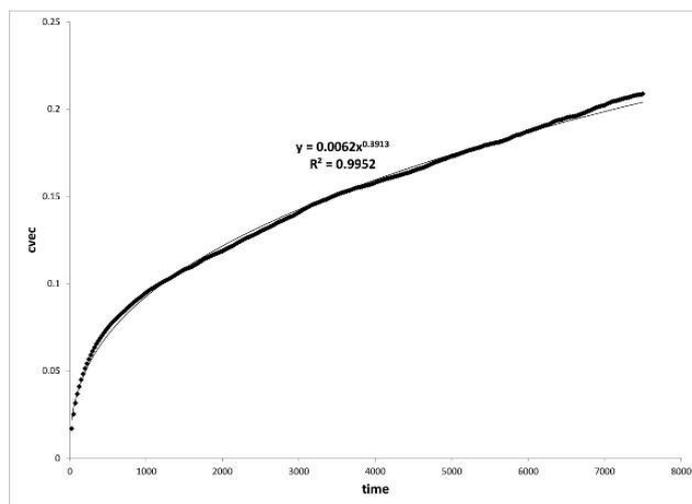


Figure 7a. $-\ln(cvec)$ quantity depending on time for a strong gel ($\epsilon_{AA} = 6$) in bulk.

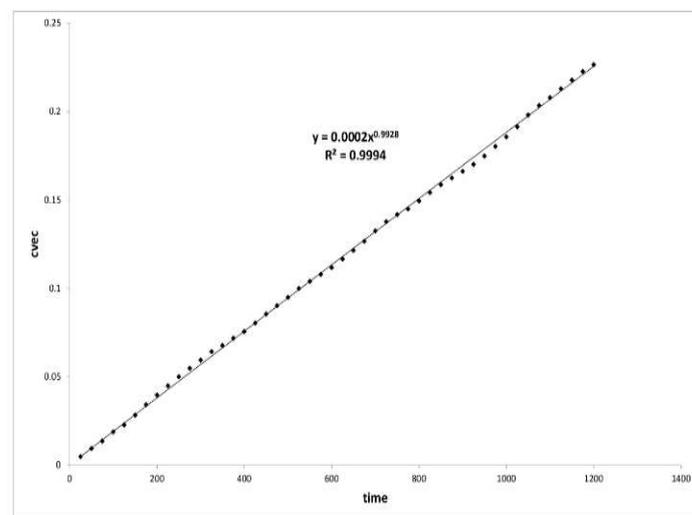


Figure 7b. *Cvec* rescaled depending on time in middle range for a strong gel ($\epsilon_{AA} = 6$) in bulk.

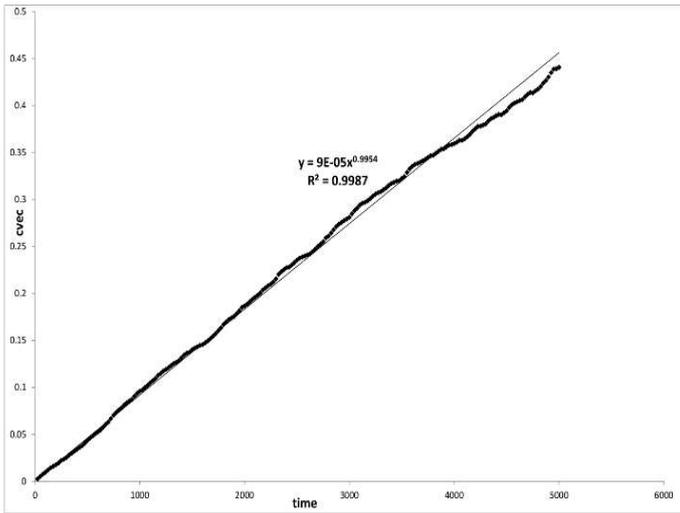


Figure 7c. Cvec rescaled depending on time in high range for a strong gel ($\epsilon_{AA} = 6$) in bulk.

Table 2. Anisotropy of the cvec components of a strong gel ($\epsilon_{AA} = 6$) in bulk conditions.

Time	Cvec	Cvec_x	Cvec_y	Cvec_z
4000	0.8664	0.8861	0.8486	0.8596
4010	0.8663	0.8860	0.8485	0.8594
4020	0.8662	0.8859	0.8484	0.8593
4030	0.8660	0.8858	0.8482	0.8592
4040	0.8659	0.8857	0.8481	0.8590
4050	0.8658	0.8856	0.8479	0.8589
4060	0.8657	0.8855	0.8478	0.8588
4070	0.8655	0.8854	0.8477	0.8587
4080	0.8654	0.8853	0.8475	0.8586
4090	0.8653	0.8852	0.8473	0.8585
4100	0.8652	0.8851	0.8471	0.8584
4110	0.8650	0.8850	0.8469	0.8582
4120	0.8649	0.8849	0.8467	0.8581
4130	0.8647	0.8848	0.8466	0.8580
4140	0.8646	0.8847	0.8464	0.8578
4150	0.8645	0.8846	0.8462	0.8577
4160	0.8644	0.8845	0.8460	0.8576
4170	0.8643	0.8844	0.8459	0.8575
4180	0.8641	0.8844	0.8457	0.8574
4190	0.8640	0.8843	0.8456	0.8573
4200	0.8639	0.8842	0.8454	0.8572
4210	0.8638	0.8841	0.8453	0.8571
4220	0.8637	0.8840	0.8451	0.8570
4230	0.8636	0.8839	0.8450	0.8568
4240	0.8634	0.8838	0.8449	0.8566
4250	0.8633	0.8837	0.8447	0.8565
4260	0.8632	0.8836	0.8446	0.8564
4270	0.8631	0.8835	0.8444	0.8563
4280	0.8630	0.8834	0.8443	0.8561
4290	0.8628	0.8833	0.8442	0.8560
4300	0.8627	0.8832	0.8440	0.8558
4310	0.8626	0.8831	0.8439	0.8557
4320	0.8625	0.8830	0.8438	0.8556
4330	0.8623	0.8829	0.8437	0.8554
4340	0.8622	0.8828	0.8435	0.8553
4350	0.8621	0.8827	0.8434	0.8552
4360	0.8620	0.8826	0.8432	0.8550
4370	0.8619	0.8825	0.8431	0.8549
4380	0.8618	0.8824	0.8430	0.8547
4390	0.8617	0.8824	0.8429	0.8546
4400	0.8615	0.8823	0.8427	0.8545
4410	0.8614	0.8822	0.8426	0.8544
4420	0.8613	0.8821	0.8425	0.8542
4430	0.8611	0.8820	0.8423	0.8541
4440	0.8610	0.8819	0.8421	0.8539

Time	Cvec	Cvec_x	Cvec_y	Cvec_z
4450	0.8609	0.8818	0.8420	0.8538
4460	0.8608	0.8817	0.8419	0.8537
4470	0.8607	0.8816	0.8417	0.8536
4480	0.8606	0.8815	0.8416	0.8535
4490	0.8605	0.8814	0.8415	0.8533
4500	0.8603	0.8813	0.8414	0.8532

About the very high interactions, which correspond to a very strong gel [33], the behavior was more complicated. In appearance, the values were similar to the previous one shown in the comparison graph, but in the transformed coordinates we saw, as reported in Figure 8a and Figure 8b, that a power-law correlation was not enough to fit all the calculated data. Following the $\epsilon_{AA} = 6$ condition we can suppose a sequence of power-law correlations with a continue modification of the parameters and a very long time to pass to the linear one.

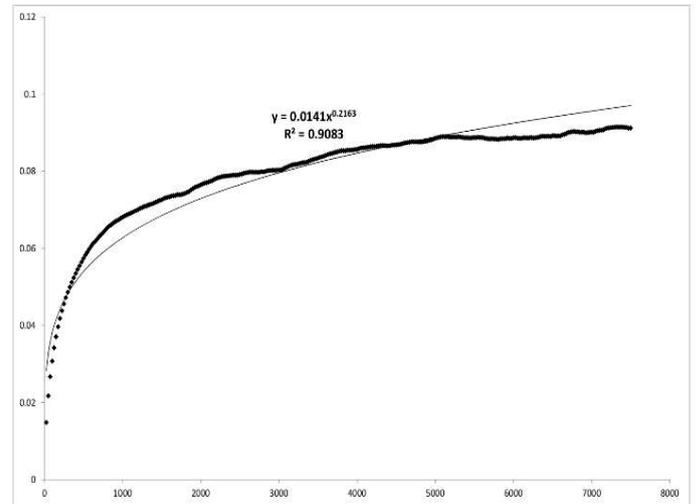


Figure 8a. $-\ln(cvec)$ quantity depending on time for a very strong gel ($\epsilon_{AA} = 7$) in bulk (range 0-7500).

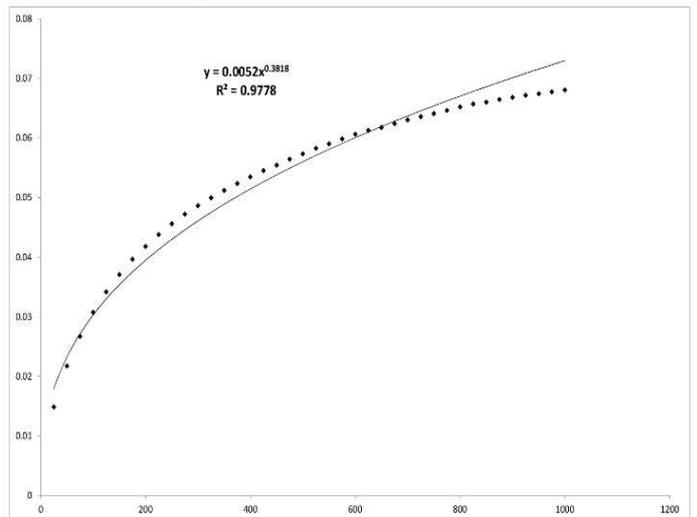


Figure 8b. $-\ln(cvec)$ quantity depending on time for a very strong gel ($\epsilon_{AA} = 7$) in bulk (range 0-1000).

The effect of an applied shear rate is different for every interaction condition. In Figure 9 we see the comparison for all the values coupled to the homopolymer case. There is no important difference for all the lines except for the two highest shear ($5 \cdot 10^{-3}$ and $1 \cdot 10^{-2}$) and this result corresponds to the one obtained in our previous paper [32] when we showed that a shear rate equal or minus to $1 \cdot 10^{-3}$ did not produce any changing to the structure of

the polymer.

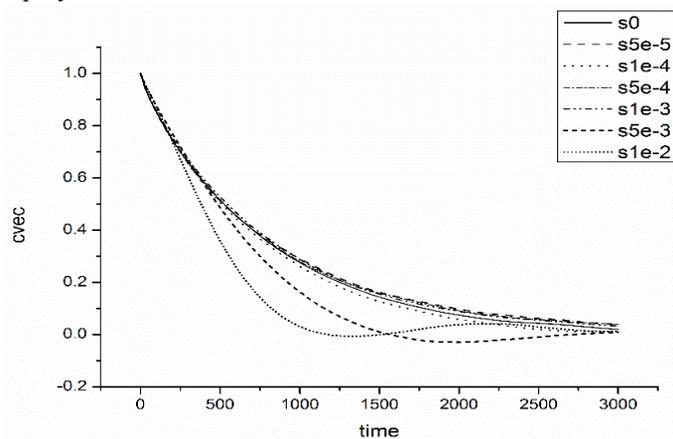


Figure 9. Influence of the shear to the correlation between *cvec* and time for a homopolymer ($\epsilon_{AA} = 1$).

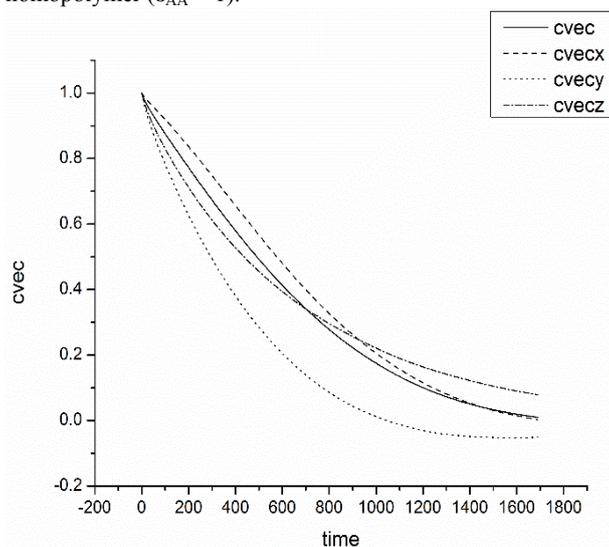


Figure 10. Anisotropy of *cvec* when a shear equal to $5 \cdot 10^{-3}$ has applied to a homopolymer.

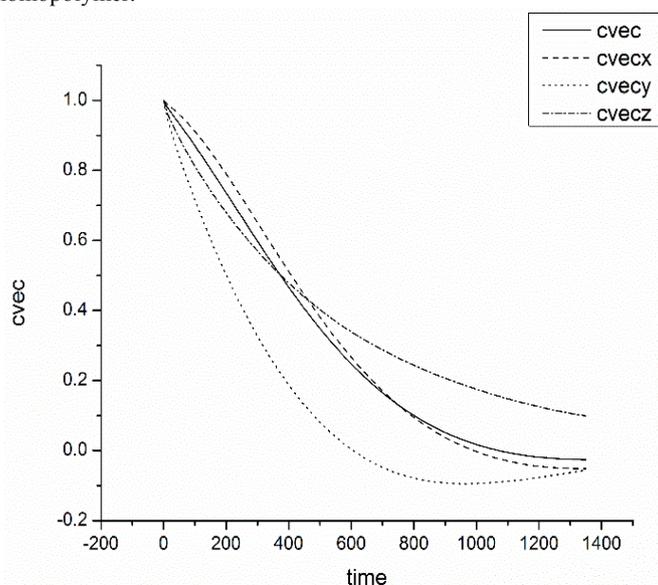


Figure 11. Anisotropy of *cvec* when a shear equal to $1 \cdot 10^{-2}$ has applied to a homopolymer.

When the shear was increased to $5 \cdot 10^{-3}$ the relaxing time decreased and above all, there was an important anisotropy that produced a major decrease along the *y* axis. This result can be explained since the shear has applied along the *x* direction against the *y* one. It is also important to observe the different behavior of

the *z* component respect to the *x* one. The last in a short time range decreases forming a negative concavity and changes after a signed time meanwhile the *z* one forms something similar to an exponential decrease (Figure 10). Since *z* is the “neutral” direction with respect to the applied shear, this result seems to be right. If the shear is $1 \cdot 10^{-2}$ the result is similar to the previous one (Figure 11) being the relaxing time of the *y* component very short, meanwhile, when the time increases there is an increase to reach a plateau.

To conclude the paragraph about the homopolymer we build up two graphs considering the average value of *cvec* transformed to the log form for the two highest shear (Figure 12a/b). We observe that a power-law correlation does not agree at all, and this means that the ungrouping is more complex than a stretched exponential.

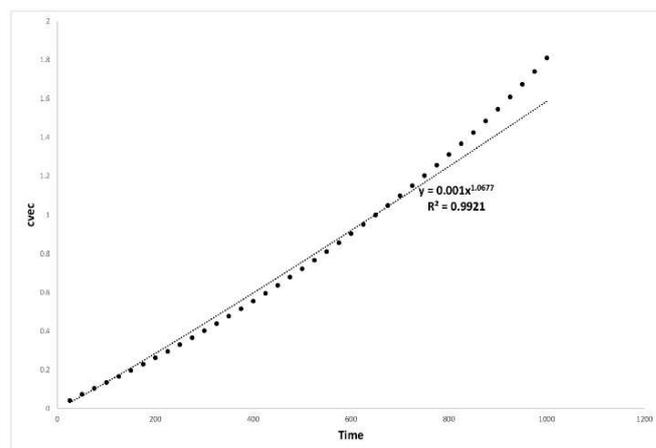


Figure 12a. *Cvec* depending on time for a homopolymer in bulk when a shear of $5 \cdot 10^{-3}$ has applied.

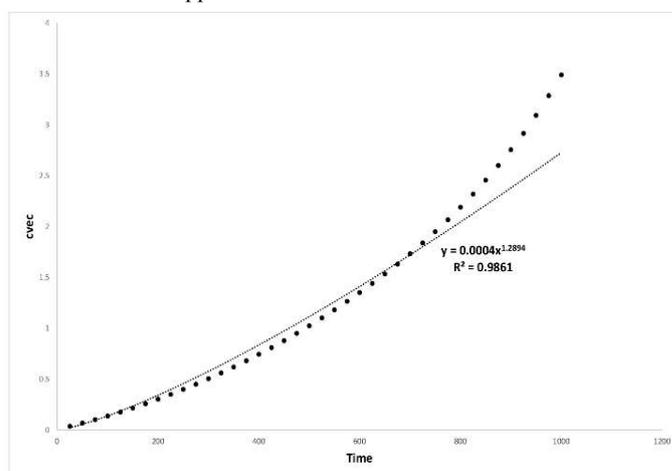


Figure 12b. *Cvec* depending on time for a homopolymer in bulk when a shear of $1 \cdot 10^{-2}$ has applied.

When the interactions were average (Figure 13) we observed no significant changing for shears equal or minus to $5 \cdot 10^{-4}$ except a light anisotropy for the *y* axes, similar to what previously described. If the shear is $1 \cdot 10^{-3}$ the anisotropy is more important but all the components decreased in stretched exponential forms (Figure 14). At least, when the shear was increased the behavior was similar to the homopolymer one: the anisotropy appeared and the ungrouping concavity changed. When the interactions were high or very high (Figure 15 and 16) two low shears of $5 \cdot 10^{-5}$ or $1 \cdot 10^{-4}$ did not produce changing on the values of the parameters, being the dependence on time similar to a bulk

condition, meanwhile the following value of $5 \cdot 10^{-4}$ created different effects. In the $\epsilon_{AA} = 6$ condition (Figure 17) there was a decrease of the relaxing time coupled to an anisotropy similar to the previously observed: the y coordinates decreased faster than the others. Instead in the $\epsilon_{AA} = 7$ case there was no changing, too.

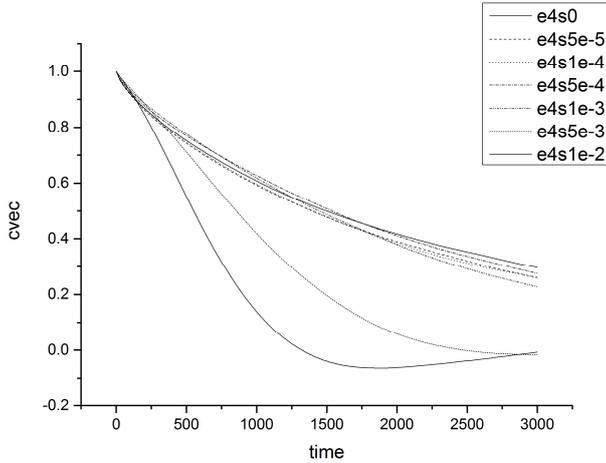


Figure 13. Influence of the shear to the correlation between cvec and time for a weak gel ($\epsilon_{AA} = 4$).

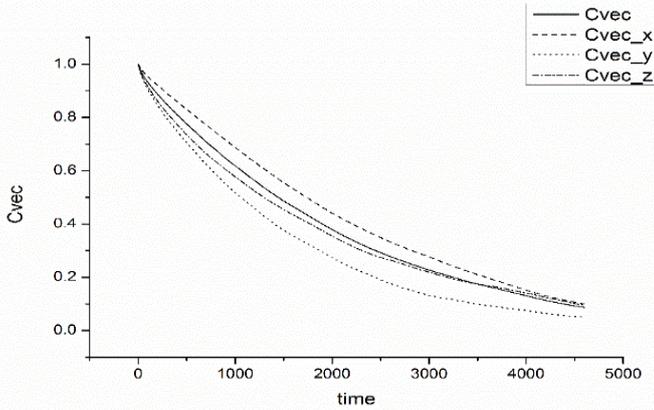


Figure 14. Behavior of cvec, both average and all Cartesian components, when a shear equal to $1 \cdot 10^{-3}$ has applied to a weak gel ($\epsilon_{AA} = 4$).

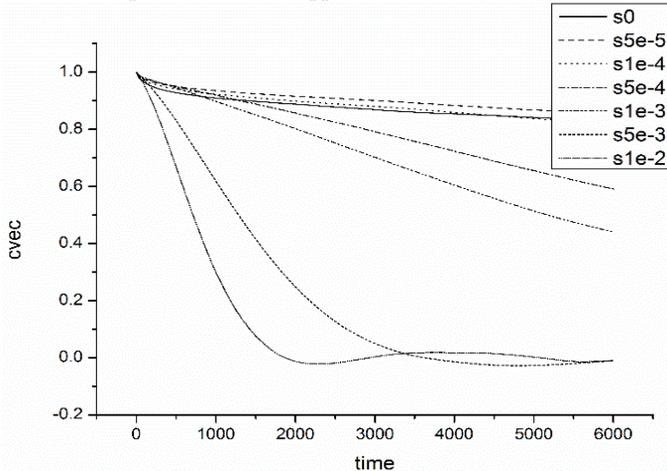


Figure 15. Influence of the shear to the correlation between cvec and time for a strong gel ($\epsilon_{AA} = 6$).

When the shear assumes a higher value the behavior is more complex and similar to the one seen in the case with average interactions: y very short relaxing time, z exponential and x double quadratic. The difference is that in this condition the x component is dominant and the average value follows the same line (Figure 18).

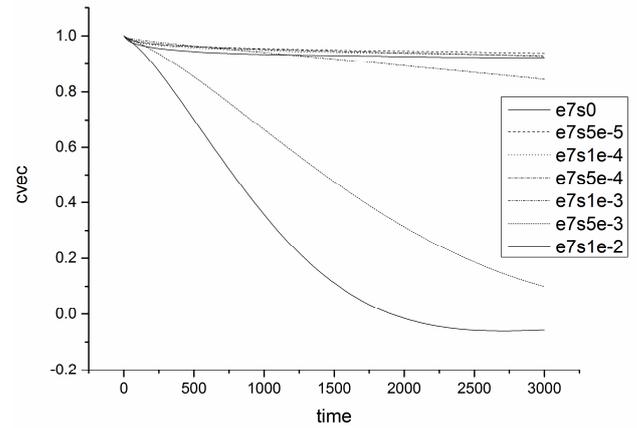


Figure 16. Influence of the shear to the correlation between cvec and time for a very strong gel ($\epsilon_{AA} = 7$).

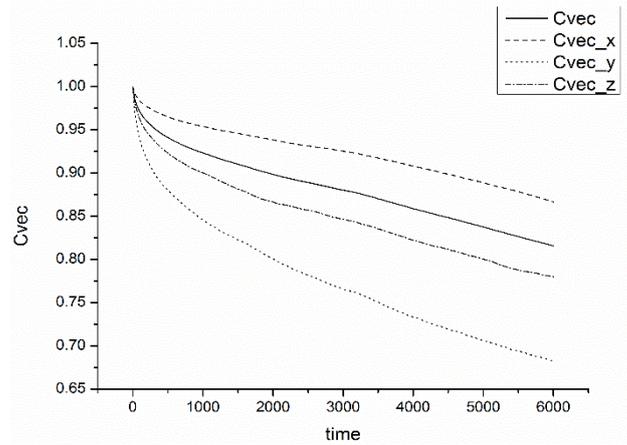


Figure 17. Behavior of cvec, both average and all Cartesian components, when a shear equal to $5 \cdot 10^{-4}$ has applied to a strong gel ($\epsilon_{AA} = 6$).

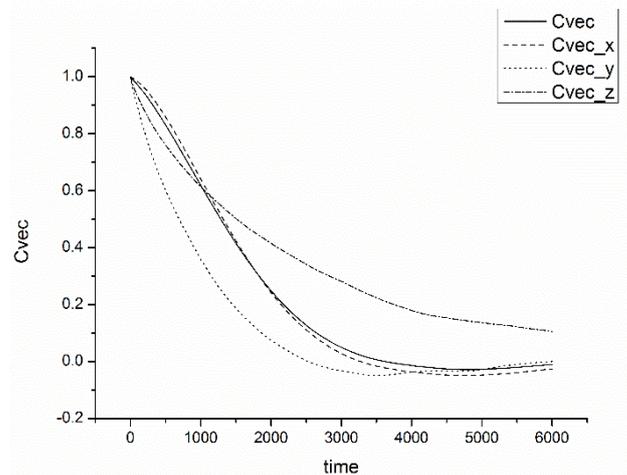


Figure 18. Behavior of cvec, both average and all Cartesian components, when a high shear has applied to a strong gel ($\epsilon_{AA} = 6$).

At least when the shear is the highest the behavior is similar and the same for the $\epsilon_{AA} = 7$ case, as shown in Figure 19.

About msd the presence of A-A interactions, which transforms the polymer to a gel, reduces the mobility and the diffusion coefficient, remaining the correlation linear (Figure 20).

It is easier to analyze the effect of the shear rate on msd, respect to cvec: a convective movement which conducts to have a quadratic form for the x. In Figures 21a,b,c,d we compare for every A-A interaction the effects of all the shear values applied. It is necessary to use a logarithmic scale on the y axis because different magnitudes are present. We show a couple of examples

(Figure 22-23) which allow us to understand the differences between two close conditions, and one more (Figure 24) to clarify the great importance of the convective movement.

It is important to observe that, being the convective movement dominant, all the quadratic fits agree better respect to the no-shear linear ones for every A-A interaction.

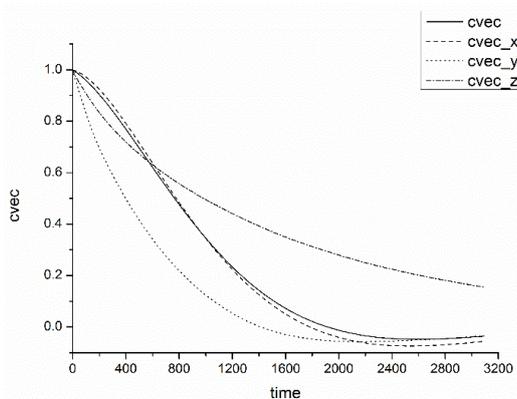


Figure 19. Behavior of cvec, both average and all Cartesian components, when a very high shear has applied to a very strong gel ($\epsilon_{AA} = 7$).

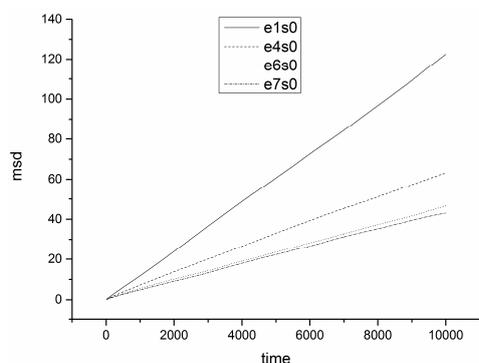


Figure 20. Influence of A-A interactions to the correlation between msd and time in no shear conditions.

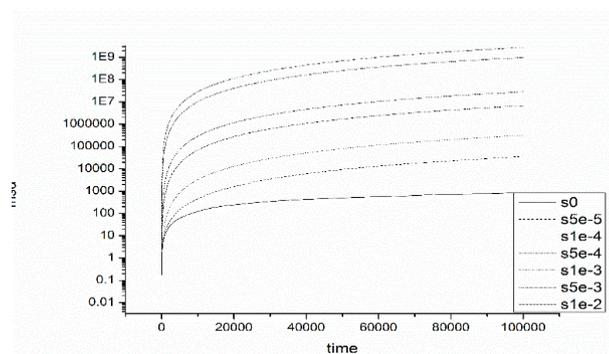


Figure 21a. Influence of the shear to the correlation between msd and time for a homopolymer ($\epsilon_{AA} = 1$).

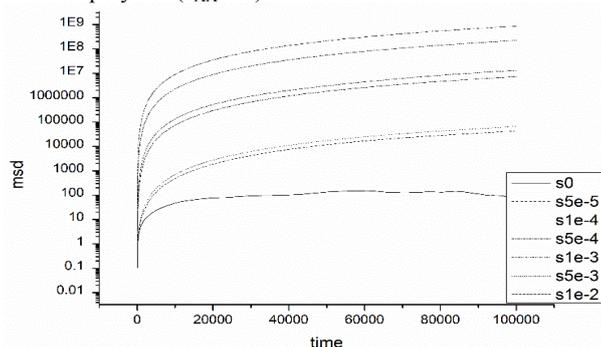


Figure 21b. Influence of the shear to the correlation between msd and time for a weak gel ($\epsilon_{AA} = 4$).

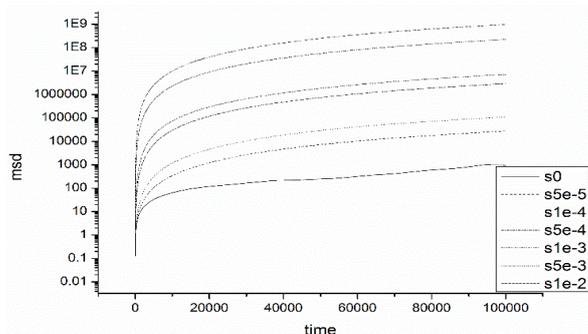


Figure 21c. Influence of the shear to the correlation between msd and time for a strong gel ($\epsilon_{AA} = 6$).

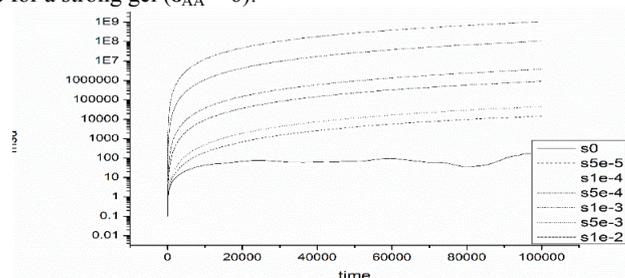


Figure 21d. Influence of the shear to the correlation between msd and time for a very strong gel ($\epsilon_{AA} = 7$).

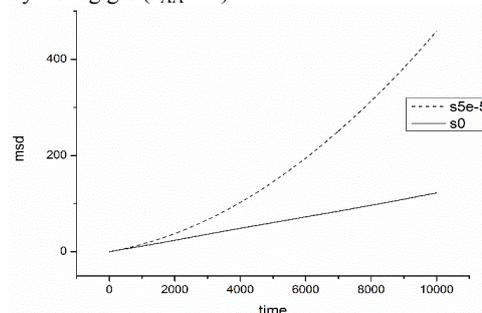


Figure 22. The presence of a very low shear applied to a homopolymer is enough to add a convective movement to the diffusive one and transform the correlation between msd and time from linear to quadratic.

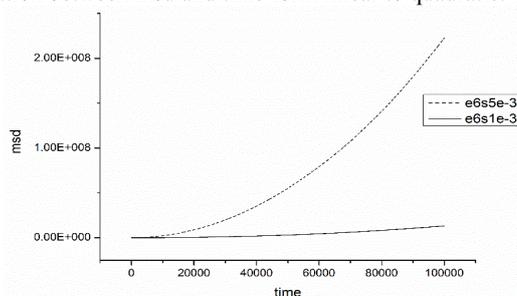


Figure 23. When a $5 \cdot 10^{-3}$ shear has applied to a strong gel instead of $1 \cdot 10^{-3}$ one, the result differs from magnitudes, remaining the correlation quadratic.

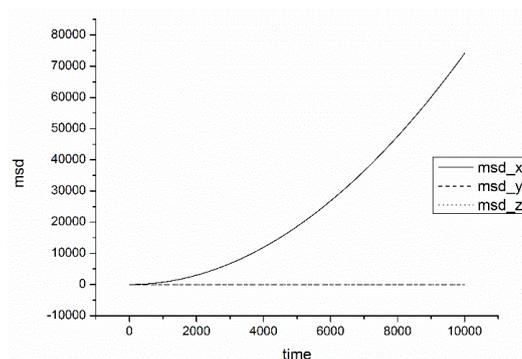


Figure 24. Different contributions of the msd components to a total in the case of $1 \cdot 10^{-3}$ shear applied to a weak gel ($\epsilon_{AA} = 4$). The y and z ones are linear, as in no shear, meanwhile the x ones becomes quadratic and differs for magnitudes.

4. CONCLUSIONS

In the present work, we evaluated in telechelic polymers the dependence on time of the dynamic quantities correlation vector and mean square displacement having different conditions of terminal beads interactions and shear rate applied.

We observed that the homopolymer in bulk conditions presented behavior very close to the one predicted from the theory but not exactly equal. In particular these differences are shown at short time ranges, when $cvec$ ungrouping was stretched exponential instead of exponential meanwhile msd was similar quadratic instead of linear.

The presence of interactions and shear rate modified the correlations in a different manner: as showed in previous papers [31-32] the A-A interactions conducted to have, instead of a polymer, a gel. Increasing the associating ability of the terminal beads, the stronger is the gel obtained and the diffusion coefficient decreases step by step and the msd too, remaining linear depending on the time. About $cvec$ in a gel the relaxing time is obviously higher than in a polymer but we observed important changes about the dependence on time: when ϵ_{AA} was equal to 4 or 6 the range where the correlation is a stretched exponential increased, being of a different magnitude comparing the last case

with the polymer one. Instead, when ϵ_{AA} assumes the 7 value the behavior is more complex and a power law, between time and $-\ln(cvec)$, is not enough to fit the calculated data.

When a shear rate has applied the material adds a convective movement, along the direction of applying, to the diffusive one transforming the relation between msd and time from linear to quadratic. The stronger is the shear the stronger is the part of the x axis to the total and the other 2 components become not relevant.

The evolution of $cvec$ is more complex: it is necessary a minimum shear to obtain a significant changing, and the value differs on the A-A interactions, similar to what obtained for the structure [32], but not equal. In general the presence of a sufficient shear decreases the relaxing time, also drastically, and for the strong and very strong gel introduces an important anisotropy among the three directions. Along the z one, that is neutral respect to the shear applied, the behavior does not modify remaining an exponential ungrouping; along the y one, there is a very short relaxing time while along the x one there is a more complex behavior. In fact we point out a double quadratic form of the shear, first negative for short times range, then positive.

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