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## LETTER TO THE EDITOR

# Electric bi-refringence of branched polymers

M Daoud† and J Klafter‡

† Laboratoire Léon Brillouin§, CEN Saclay, 91191 Gif-sur-Yvette cedex, France

‡ Tel Aviv University, Chemistry Department, 69978 Ramat Aviv, Israel

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**Abstract.** We calculate the transient electric bi-refringence  $B(t)$  when an electric field is applied to polarizable, randomly branched, polymers in a dilute solution. We find that it relaxes with time as a stretched exponential,  $B(t) \sim \exp(-t^\alpha)$ . The exponent  $\alpha$  is calculated both for a single mass  $N$  and for the very broad, percolation-like distribution of masses that is usually obtained when one synthesizes such polymers. In the former case, such experiments would show the difference between the statistics of lattice animals and that of swollen polymers. The latter case exhibits the influence of the mass distribution on the long time relaxation properties. The calculations are made both in the Zimm approximation for the hydrodynamics, and in the Rouse limit, where screening of the hydrodynamic interaction occurs at large distances for the stretched configurations.

The static and dynamic properties of randomly branched polymers have been under strong investigation these last few years [1-6]. Their fractal structure was observed by light [7] and neutron [8] scattering experiments as well as by viscoelastic measurements [9, 10]. Several modes of synthesis were used, such as polycondensation of multifunctional units [11, 12], crosslinking of pre-existing linear polymers by irradiation [13] or by end-linking [14] and, very recently, biopolymers [15]. The most important result in these studies is that it seems that percolation is an important universality class for the description of the synthesis of such branched polymers. As a result, there is a natural distribution of molecular weights, similar to the cluster distribution function in percolation [16], which is extremely wide. This is called polydispersity. It increases as one tries to get larger polymers by approaching the gelation threshold. This remains valid when one adds excess solvent to the preformed polymers, so that the resulting solution is dilute. In what follows, we will consider the latter case. Thus the various macromolecules are assumed to be dispersed in an excess of solvent and are far from each other. The solvent is assumed to be a good solvent [17]. Because of the polydispersity, one does not observe directly the fractal dimension of the polymers, but rather an effective dimension that is related both to the dimension of each macromolecule and to the exponent of the (number) distribution  $P(N, \varepsilon)$ . The latter is the number of polymers made of  $N$  monomers at a distance  $\varepsilon = |p - p_c|$  from the threshold. It has been demonstrated by several groups that under these conditions, the effective fractal dimension of the polydisperse ensemble of polymers is indeed different from that of the individual polymers, given in terms of lattice animals [18].

Summing up these results, one may say that a dilute solution of randomly branched polymers in a good solvent is very polydisperse with a distribution  $P(N, \varepsilon)$  of molecular

§ Laboratoire commun CNRS-CEA.

weights, and that each polymer has the same fractal dimension  $D_0$  as a lattice animal. Thus the average radius  $R(N)$  of a polymer is related to its number  $N$  of monomers by the usual relation:

$$N \sim R(N)^{D_0}. \quad (1)$$

We are interested in finding out whether the swollen macromolecules actually follow the same statistics as the lattice animals or not. This may be characterized for instance by the probability  $G(R)$  of finding any two ends at a distance  $R$ . In what follows, we discuss a possible experimental technique related to the Kerr effect, that allows for the measurement of the large-distance behaviour of such a function. This method has been recently used by Degiorgio *et al* [19] who studied the large distance behaviour of  $G(R)$  for linear chains. They found a characteristic stretched exponential behaviour for the relaxation of the electric bi-refringence that could be directly related to the exponential form of  $G(R)$ . We would like to extend their results to the case of randomly branched polymers. One may think of two possible types of experiments, either with the natural, polydisperse, distribution that we discussed above, or with a monodisperse solution, obtained by suitable fractionation of the previous one. Such fractionation has already been made on different samples [8, 20, 21] in order to study their fractal structure.

In a typical transient electric bi-refringence experiment [22], one applies a rectangular electric pulse to a polarizable polymer in a dilute solution and studies the transient evolution of the bi-refringence towards equilibrium. The advantage of the method is that it tests directly all the possible conformations of a polymer, including the large, improbable fluctuations included in the distribution  $G(R)$ . As explained by Degiorgio *et al*, the relaxation of the bi-refringence  $B(t)$  as a function of time in the transient regime is directly related to the distribution of distances:

$$B(t) = \int dR S(R) G(R) e^{-t/\tau(R)} \quad (2)$$

where  $S(R)$  is a signal function that has at worst a power-law behaviour, and  $\tau(R)$  the relaxation time of a polymer with given distance between surface monomers. The precise form of  $S(R)$  is not important for our purpose because we will be interested only in the long-time behaviour of  $B(t)$ . Let us note, however, that its precise form would be very interesting for the study of short-time behaviour, and may allow the measurement of the short-distance behaviour of  $G(R)$ . The latter involves the exponent  $\theta$  (or  $\gamma$  for linear chains) that has not been measured so far. As we will see, the long-time behaviour is governed by stretched exponentials, and thus for our purpose, as long as this signal function does not have any exponential part, we may ignore safely its variation.

The average relaxation time  $\tau(N)$  of a polymer in a dilute solution has been studied. In such dilute solutions, it is known that hydrodynamic interactions [23, 24] have to be taken into account, and that each macromolecule follows a Zimm-type dynamics. Thus the average characteristic time  $\tau(N)$  for a macromolecule made of  $N$  monomers, with average radius  $R(N)$  is [1, 24]

$$\tau(N) \sim R(N)^3. \quad (3a)$$

The most direct hypothesis about the relaxation time of the stretched configurations is to assume that relation (3a) holds generally for every configuration with distance

$R$ . Therefore we have, for any  $R$

$$\tau(R, N) \sim R^3. \quad (3b)$$

Some years ago however, Pincus [25] showed that the relaxation time  $\tau_p$  for a polymer chain stretched by an external force should rather follow a Rouse-type dynamics. This is because a screening of the hydrodynamic interactions occurs in the stretched configurations. If we assume that such an effect is also present for the large fluctuations, it is possible to find the characteristic time by assuming a scaled form for the time:

$$\tau(R, N) = N^{3/D_0} f(R/N^{1/D_0}). \quad (4)$$

The  $R$  dependence of the Rouse time is known. Assuming that  $f(x)$  in relation (4) behaves as a power-law, we get

$$\tau_p(R, N) \sim R^{2+D_0} N^{(1-D_0)/D_0} (R \gg N^{1/D_0}). \quad (3c)$$

However, the experimental results of Degiorgio *et al* [19] seem to be better fitted by the Zimm time. We will therefore present our results both in the Zimm and Rouse approximations, which correspond to relations (3b) and (3c) respectively.

The final point to be discussed in relation (2) is the distribution  $G(R)$ . For a given mass  $N$ , the above-mentioned  $R(N)$  is only an average over all the configurations that may be assumed by a polymer. We know from previous studies that because of the wide fluctuations, there is a distribution of distances  $G(R)$  which was carefully studied for linear chains [1, 26]. The latter study may be generalized directly to the branched polymers which we are considering. This is because the chemistry is already performed, as in the self-avoiding walk problem. Thus the only fluctuations that are allowed to any given polymer are related to stretched configurations. This implies that the large-distance behaviour of the distance distribution  $G(R)$  is related to the fractal dimension  $D_0$  of the polymer. Following the same arguments as for linear chains, we find, for large distances:

$$G(R) \sim \exp[-(R^{D_0}/N)^{1/(D_0-1)}] \quad R \gg R(N). \quad (5)$$

Equation (5) is different from what is expected in the lattice animal problem. A different exponent is obtained then, and is related to the various chemical configurations that are possible rather than to the distance fluctuations at given chemistry.

In a polydisperse solution, one has to take into account, in addition to this distribution of distances for a given value of  $N$ , a distribution of molecular weights: the probability of finding a polymer made of  $N$  monomers is, following Stauffer [16]:

$$P(N, \varepsilon) \sim N^{-\tau} e^{-N\varepsilon^{1/\sigma}} \quad (6a)$$

where the exponents  $\tau$  and  $\sigma$  are percolation exponents. Introducing the  $z$ -average molecular weight [17]

$$N_z = \frac{\int N^3 P(N, \varepsilon) dN}{\int N^2 P(N, \varepsilon) dN} \sim \varepsilon^{-1/\sigma} \quad (7)$$

and inserting (7) in (6a), we get

$$P(N, \varepsilon) \sim N^{-\tau} e^{-N/N_z}. \quad (6b)$$

The relaxation of the bi-refringence may be readily calculated both for a mono-disperse and a polydisperse solution. Let  $B_N(t)$  and  $B_p(t)$  be the functions in these respective cases. They are related through

$$B_p(t) = \int B_N(t) P(N, \varepsilon) dN. \quad (8)$$

In the case of a fractionated sample with a single molecular weight  $N$ , we have, using the previous results and the Zimm assumption

$$B_N(t) = \int S(R) \exp[-(R^{D_0}/N)^{1/(D_0-1)}] \exp(-t/R^3) dR. \quad (9)$$

The integral is estimated by the steepest-descent method. We find

$$B_N(t) \sim \exp[-(t/N^{3/D_0})^{D_0/(4D_0-3)}] \quad (10a)$$

and, using the accepted value,  $D_0 = 2$  for  $d = 3$ , we get in the Zimm case and for a monodisperse solution:

$$B_N(t) \sim \exp[-(t/N^{3/2})^{2/5}] \quad (\text{Zimm}). \quad (10b)$$

In the other limit, if we accept the idea of screening of the hydrodynamic interactions for the extended fluctuations, the dynamics is a Rouse-type instead of the Zimm approach. The characteristic relaxation time is now given by relation (3c) instead of equation (3a). For  $d = 3$ , we have  $D_0 = 2$ , and

$$\tau_p(R) \sim R^4 N^{-1/2}.$$

Using the same approach as above, we get

$$B_N(t) \sim \exp[-(t/N^{3/2})^{1/3}] \quad (\text{Rouse}). \quad (10c)$$

Two points are worth being discussed when one compares equations (10b) and (10c). The first one is that the change in the hydrodynamic assumption implies a large change in the exponent of the stretched exponential, which varies from 0.4 when hydrodynamic interactions are present, in the Zimm case, to  $\frac{1}{3}$  in the Rouse case, when no hydrodynamic interactions are present beyond a distance of the order of the equilibrium radius of the polymer. That the Rouse dynamics is slower is an expected result because (i) the solvent motion enhances the polymer motion in the Zimm case, and (ii) the friction coefficient increases linearly with  $N$  in the Rouse case. The difference in the values of the exponents is amenable to experimental observation. Such an experiment on a fractionated sample is thus interesting both in order to check the value of the exponent in the distribution function  $G(R)$ , and the kind of dynamics that governs the stretched conformations of a branched polymer.

The second point to be noted is that both characteristic times in the Zimm and Rouse cases, relations (10b and 10c), behave as the average relaxation time  $\tau(N)$ , relation (3a). Namely, although the stretched configurations have a slower, Rouse-like, dynamics, the average relaxation time is still consistent with a Zimm dynamics, as it should in a dilute solution.

As discussed above, when no special fractionation is made, the solution is naturally polydisperse, and the measured bi-refringence  $B_p(t)$  is the average of the above result on the entire distribution of molecular weights, relation (6b):

$$B_p(t) = \int B_N(t) N^{-\tau} e^{-N/N_z} dN. \quad (11)$$

Calculating again the above integral by steepest descent and neglecting the power-law prefactors, we get in the Zimm case

$$B_p(t) \sim \exp[-(t/N_z^{3/2})^{1/4}] \quad (\text{Zimm}). \quad (12a)$$

Similarly, using relation (10c), we get in the Rouse case

$$B_p(t) \sim \exp[-(t/N_z^{3/2})^{2/9}] \quad (\text{Rouse}). \quad (12b)$$

Relations (12) are expected to hold for large times, larger than  $N_z^{3/2}$ . For shorter times power-law corrections are expected to be present. However, because we do not know the precise form of the signal function  $S(R)$ , relation (2), it is not possible to provide explicit forms. The various exponents are summarized in table 1, which shows that there is a significant difference between the respective values for the mono- and polydisperse cases. The stretched exponentials derived above result from a broad distribution of relaxation times  $\tau(R)$ . It has been shown that such large distributions are common to a wide range of complex systems, where similar stretched exponential behaviour is observed [27].

**Table 1.** The exponents for the time dependences for dilute solutions of polymers. Mono-disperse corresponds to fractionated samples, polydisperse to the natural polydispersity. Zimm corresponds to the presence of backflow effects in the solvent and Rouse to the screening of the latter for stretched configurations. We included the linear chain case, for which Zimm is the Degiorgio result.

	Zimm	Rouse
Branched monodisperse	$\frac{2}{5} = 0.4$	$\frac{1}{3}$
Branched polydisperse	$\frac{1}{4}$	$\frac{2}{9} = 0.22$
Linear	$\frac{5}{11} = 0.45$	$\frac{15}{37} = 0.41$

We considered the transient electric bi-refringence of randomly branched polymers in dilute solutions. Because this technique probes all the configurations of a macromolecule, it allows for the determination of the distribution function  $G(R)$ . The obtained relaxation patterns are stretched exponential. We calculated the exponents of the time dependences both for a monodisperse polymer, corresponding to a fractionated sample, and for the whole distribution of molecular weights. The latter was previously shown to be identical in most cases to the distribution of percolation clusters in the percolation problem. The calculations were made under two different assumptions. In the first one, following Degiorgio *et al* [19], we assumed that the relaxation of stretched configurations follows a Zimm-type hydrodynamics, with backflow effects present. In the second one, we assumed, following previous work by Pincus on stretched polymers, that there are screening effects at distances larger than the average radius of the macromolecule. This second assumption corresponds to a Rouse-type dynamics for the stretched configurations. The results are summarized in table 1. Although we think that the second assumption should provide a better description, the Degiorgio experimental results on linear polymers [22] seem to favour the first one. We have included in table 1 the corresponding exponents for linear chains. We believe that it would be very interesting to check these time dependences both in the mono- and polydisperse cases. In the former, we assumed that the behaviour of the distribution is related to the stretched configurations of a polymer. This implies that the statistics of branched polymers should be different from that of a lattice animal, although the fractal dimensions are identical in both problems. It would also be very interesting to observe the slowing down of the relaxation related to the presence of very large polymers, with sizes bigger than the  $z$ -average size  $N_z$  that are usually observed in static experiments.

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