

# Direct Observation of Odd–Even Effect in Dilute Polymeric Solutions: A Time-Resolved Fluorescence Anisotropy Study

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The odd–even effect is demonstrated, for the first time, in dilute polymeric solutions of polyethers, consisting of substituted luminescent quinquenyl units which are connected by flexible aliphatic chains of 7–12 methylene groups. The effect, which is demonstrated by means of steady state and time resolved fluorescence anisotropy, has been attributed to the different mutual orientation of the luminescent dipoles, in the odd (7, 9, 11) and even (8, 10, 12) polymers. Namely, as the temperature of the solution is lowered the flexible aliphatic chains adopt the nearly all-staggered lowest energy conformation, which results in different mutual orientations of the fluorophores in the two types of polymers.

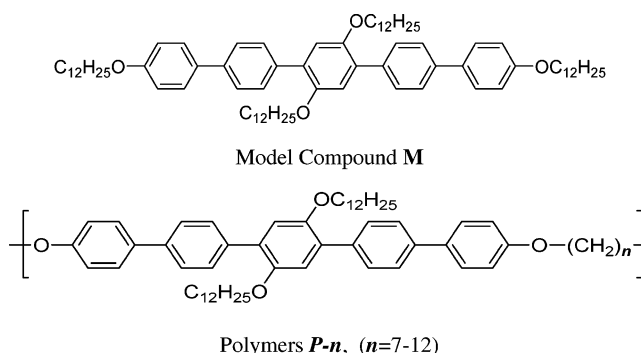
## Introduction

The so-called “odd–even” effect of the number of methylene groups in aliphatic chains is a well-known and extensively demonstrated phenomenon.<sup>1–4</sup> In the overwhelming majority of these cases this effect has been observed in the solid state and has been mainly attributed to packing differences in the crystal structure<sup>5</sup> between chains having an odd or even number of methylene groups. Actually most known series of compounds having alkyl chains with variable numbers of methylene groups  $[-CH_2]_n-$  display an odd–even effect in their phase transition temperatures,<sup>1</sup> optical characteristics, etc.<sup>2–5</sup> For these solid-state affected characteristics, many experimental techniques have been employed, all pointing out to the different adopted shapes of alkyl chains in their all-staggered conformations.<sup>6</sup> Especially in those cases in which mesogenic units are separating subsequent aliphatic spacers it has been long assumed that the final packing ability of the mesogenic parts in one or the other conformation will eventually control the final bulk properties of the material.

Recently, the odd–even dependence of the glass transition temperature ( $T_g$ ), a property that is mainly related to the chain mobility, was observed in rigid flexible aromatic aliphatic polyethers.<sup>7–10</sup> Moreover, by means of vibrational circular dichroism, the odd–even effect has been directly demonstrated in solution, for the case of some chiral alkyl-alcohols.<sup>11</sup>

The origin of the odd–even effect, even in the bulk state, still attracts research interest both experimentally<sup>12</sup> and theoretically<sup>13</sup> since it has been recognized that a deep understanding of the mechanism involved in this phenomenon will lead to a further fundamental insight of the respective physical properties.<sup>12</sup> In this line, a theoretical study of the conformation of single chains of a segmented polyurethane was performed.<sup>14</sup> The chains were composed of a rigid aromatic segment and a

## SCHEME 1



flexible aliphatic spacer and since only single chains were considered the effects of the intermolecular interactions were excluded. The calculations showed a strong odd–even effect of the spacer length on the orientation of the single chains, which was interpreted as an effect of local specific conformational features of the chains.

In the present article we wish to report our findings on the clear-cut demonstration of the odd–even effect in dilute polymeric solutions of luminescent polyethers consisting of substituted quinquenyl units, connected by flexible aliphatic chains of 7–12 methylene groups. Polymers with 7, 9, or 11 methylene groups in the aliphatic spacer are referred to as odd polymers, while those with 8, 10, or 12 methylenes are referred to as even polymers. The experimental method employed was based on measurements of steady-state and time-resolved fluorescence anisotropy.

## Experimental Section

**Synthesis.** The model compound (**M**) and polyethers **P-n** (Scheme 1) were prepared according to literature procedures.<sup>8</sup> Their structural perfection was examined by means of <sup>1</sup>H and <sup>13</sup>C NMR spectroscopy, while the molecular characteristics of the polymers were investigated by using gel permeation chromatography and are given in Table 1. Note that the

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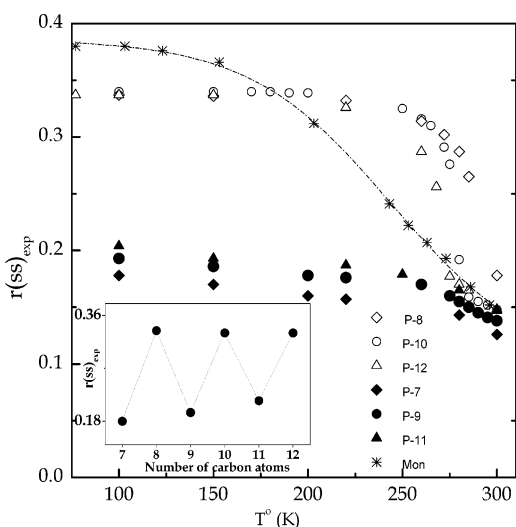
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**TABLE 1: Molecular Characteristics of Polyethers P-*n* (*n* = number of methylene units of the aliphatic spacer)**

<i>n</i>	$M_n^a$	$M_w^a$	$M_w/M_n^a$
12	67 040	130 540	2
11	49 000	99 880	2
10	43 000	84 000	2
9	33 130	65 240	2
8	70 730	155 800	2.2
7	18 870	58 260	3.1

<sup>a</sup> From gel permeation chromatography (GPC), versus polystyrene standards, chloroform as eluent, at room temperature.  $M_n$ ,  $M_w$ : number and weight average molecular weights, respectively.  $M_w/M_n$ : polydispersity.



**Figure 1.** Experimental values of steady-state fluorescence anisotropy vs temperature. Inset:  $r(ss)_{\text{exp}}$  vs number of methylene groups of the flexible aliphatic chain;  $T = 100$  K.

**TABLE 2: Photophysical Parameters of Odd and Even Polymers at  $T = 100$  K**

polymer	$\Theta$ (ps) <sup>a</sup>	$r_0^a$	$r_\infty^b$	$r(ss)_{\text{exp}}$	$r(ss)_{\text{calc}}^c$	$k_{\text{cet}}^d$ (ns <sup>-1</sup> )
P-7	440	0.36	0.13	0.18	0.19	<i>e</i>
P-9	500	0.36	0.13	0.20	0.20	<i>e</i>
P-11	760	0.38	0.14	0.22	0.23	<i>e</i>
P-8	330	0.40	0.34	0.34	0.34	1.84
P-10	400	0.40	0.34	0.34	0.34	1.43
P-12	570	0.38	0.34	0.34	0.34	0.91

<sup>a</sup> Obtained from fit. <sup>b</sup> Obtained from experimental data (see Figure 3). <sup>c</sup> Calculated from eq 5. <sup>d</sup> Calculated from eq 4. <sup>e</sup> Values for odd polymers are not shown since the fits for  $i > 3$  were not satisfactory.

polydispersities of **P-7** and **P-8** are somewhat different from those of the other polymers; however, the results do not seem to have been affected, since they are in line with the corresponding parameters of the other polymers, as shown in Figure 1 and Table 2. Recall that similar behavior, viz., independence of the properties related to the odd–even effect, from the polymer MW (above a critical MW), has been observed, e.g., in melting temperature, glass transition temperature,<sup>6</sup> etc.

Static fluorescence anisotropy,  $r(ss)_{\text{exp}}$ , was measured with a Perkin-Elmer LS 50B spectrometer, with an estimated experimental fluctuation ca.  $\pm 0.015$  ( $\pm 3.7\%$ ). Time-resolved fluorescence anisotropy,  $r(t)$ , defined according to eq 1, was measured by using the time-correlated single photon counter FL900 of Edinburgh Instruments. In eq 1  $D(t)$  and  $S(t)$  are the

$$r(t) = \frac{D(t)}{S(t)} = \frac{GI_{VV}(t) - I_{VH}(t)}{GI_{VV}(t) + 2I_{VH}(t)} \quad (1)$$

so-called difference and sum functions,  $I_{VV}$  is the fluorescence intensity when the excitation and emission polarizers are parallel and  $I_{VH}$  is for mutually perpendicular polarizers, and  $G = I_{HH}(t)/I_{HV}(t)$  is a correction factor dependent on the emission wavelength, while the excitation was horizontally polarized in both cases. Excitation and emission wavelengths were set at 350 nm and 420 nm, respectively.

The main solvent used was 2-methyltetrahydrofuran (2-MTHF, Aldrich), which is a good solvent for these polymers and also forms optically transparent glass down to at least 100 K. Other solvents, such as chloroform, dichloromethane, tetrahydrofuran, and toluene, which do not form glasses, were used in supplementary experiments down to 220 K. All the solvents used in this study were purchased from Aldrich and were purified by passage through an alumina column followed by distillation in the presence of  $\text{LiAlH}_4$ . All the measurements were performed in the concentration range  $3.3 \times 10^{-6}$  to  $5.0 \times 10^{-7}$  M in which aggregation of the solute was not observed.

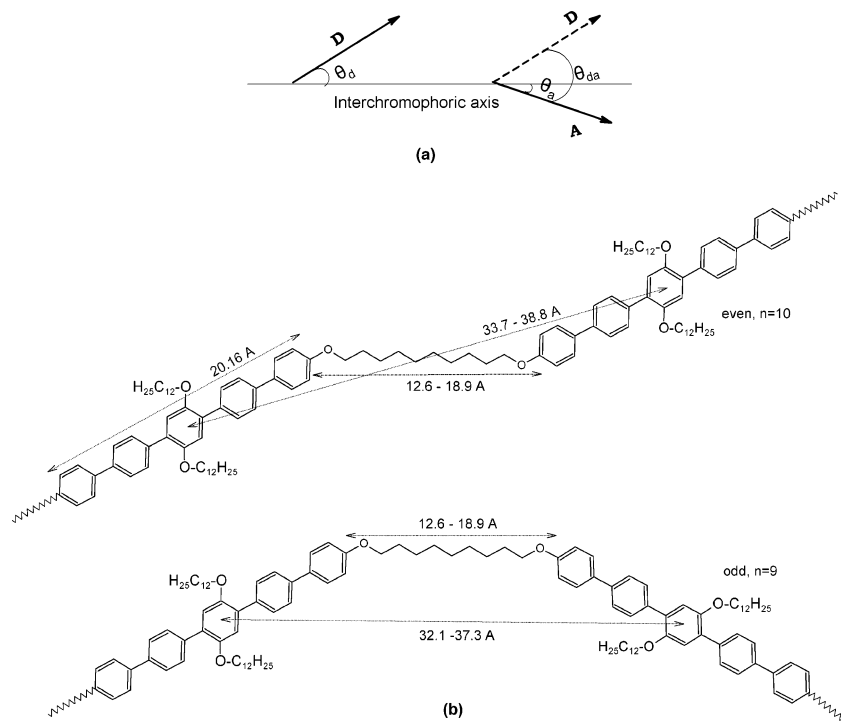
## Results and Discussion

The particular polymeric series chosen for this study can be considered as model systems for the examination of the effect of the conformational changes of the aliphatic spacer, in the bulk state as well as in solution. These polymers combine adequate solubility with the presence of highly luminescent rigid parts connected with the variable length aliphatic spacers. Thus, the specific arrangements of the luminescent *p*-quinquephenyl units can be well defined and changes of their orientation as well as intra- or interchain interactions among them can be detected by using various steady state<sup>15,16</sup> or time-resolved spectroscopic techniques.<sup>17–23</sup>

**Static Fluorescence Anisotropy.** Figure 1 shows the variation of the steady-state fluorescence anisotropy of **P-*n*** for  $n = 7–12$ , from 300 to 100 K, as well as the corresponding values of the monomer **M** (Scheme 1). Note that the  $r(ss)_{\text{exp}}$  value of the monomer varies smoothly from 0.15 at room temperature to 0.38 at 100 K. The fact that at the low temperature, when molecular tumbling has ceased, the  $r(ss)_{\text{exp}}$  of the monomer has not reached the theoretical value of 0.4 indicates that the absorption and emission dipoles of the fluorophore (*p*-quinquephenyl) are not collinear but instead they form an angle of ca.  $10^\circ$ . On the other hand, the fluorescence anisotropy of the polymers at low temperature is lower than that of the monomer, despite the lack of molecular motions. This is interpreted as evidence of electronic excitation energy transfer between neighboring fluorophores in the frozen polymers, which occurs via the well-known Förster mechanism (resonance interactions). According to this mechanism the rate of the electronic energy transfer  $k_{\text{cet}}$  between two randomly oriented identical groups, the one termed donor (d) and the other acceptor (a), separated by a distance  $R$  is given by eq 2. In this equation  $\tau_f$  (found here equal to about 1 ns) is the fluorescence lifetime of the fluorophore (*p*-quinquephenyl), which in the present case acts as donor as well as acceptor of the electronic excitation (homotransfer).  $R_0$  is the so-called Förster distance, at which the rate for energy transfer equals the rate for all other deexcitation processes of the donor. Among other parameters,

$$k_{\text{cet}} = \frac{1}{\tau_f} \left( \frac{R_0}{R} \right)^6 \quad (2)$$

$R_0$  depends on the orientation factor  $\kappa^2$ , which is given by eq 3, where the angles  $\theta_{da}$ ,  $\theta_d$ , and  $\theta_a$  determine the relative orientation



**Figure 2.** (a) Angles involved in eq 3. (b) Structures of the all-staggered conformation of odd and even polymers. Distances in Å.

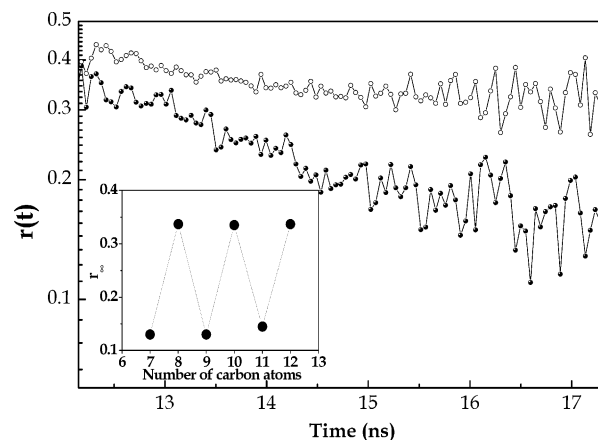
of the donor and acceptor dipole moments as shown in Figure 2. For random orientation between donor and acceptor dipoles,

$$\kappa^2 = (\cos\theta_{da} - 3 \cos\theta_d \cos\theta_a)^2 \quad (3)$$

$\kappa^2$  is usually taken equal to  $2/3$ . Assuming such random orientation, we have calculated  $R_0$  for our system as equal to 19 Å. However, when there is a fixed donor–acceptor orientation and in order to take care of the factor  $2/3$  for random orientation, eq 2 becomes eq 4. Evidently,  $k_{\text{cet}}$  in eq 4 depends on  $R$ , the donor–acceptor dipole distance, and also on the three angles  $\theta_{da}$ ,  $\theta_d$ , and  $\theta_a$ .

$$k_{\text{cet}} = \frac{3}{2} \frac{\kappa^2 (R_0)^6}{\tau_f (R)^6} \quad (4)$$

Concerning Figure 1, there are two important points deserving special attention. First, in both the odd and the even polymers the value of  $r(\text{ss})_{\text{exp}}$  shows a sudden change around 265–275 K, while similar behavior is not observed in the monomer, and second, below this temperature  $r(\text{ss})_{\text{exp}}$  exhibits a sharply different behavior in the two types of polymers (odd and even). The first observation suggests that at ca. 265–275 K a temperature induced change in the conformation of the polymers occurs, which drastically affects the excitation energy transfer between neighboring fluorophores, particularly in the case of the even polymers, where the change is dramatic. The second observation indicates that below 265 K, totally different orientational relationships between the dipoles of the fluorophores prevail in the odd and even polymers. More specifically, Figure 1 shows that from 300 K to ca. 275–280 K,  $r(\text{ss})_{\text{exp}}$  is the same, viz., 0.15–0.16, for all polymers (and the monomer); below this temperature, however, the fluorescence anisotropies of the even polymers rise from 0.15 to ca. 0.34 within the temperature range 275–265 K and then remain nearly constant down to the lowest temperature of our measurements, viz., 100 K. On the contrary, the  $r(\text{ss})_{\text{exp}}$  values of the odd polymers, despite the sudden (albeit small) increase at 275–265 K, rise

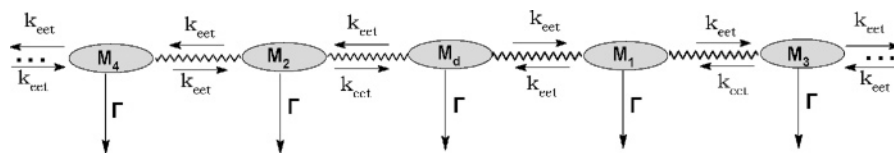


**Figure 3.** Decay of time-resolved fluorescence anisotropy ( $T = 100$  K) of one odd and one even polymer (P-12 upper data, P-11 lower data), before reconvolution. Inset:  $r(\text{ss})$  vs number of methylene groups in the flexible aliphatic chain.

only slightly, from ca. 0.15 at 300 K to ca. 0.18–0.2 at 100 K. Note that the different behavior between the odd and even polymers is also clearly discernible in the experimental data of Figure 3, where the time dependence of the fluorescence anisotropy  $r(t)$  is shown for **P-11** and **P-12**. Moreover in the monomer, in which energy transfer cannot occur and therefore any depolarization is due only to molecular tumbling,  $r(\text{ss})_{\text{exp}}$  rises smoothly as the temperature is lowered and the viscosity of the solvent increases.

Such different behavior of the fluorescence anisotropies between the odd and even homologues of these polymers may be rationalized in terms of the lowest energy conformation of the aliphatic spacer, which, in the ideal case, is the all staggered arrangement of the methylene groups, as shown in Figure 2b. Thus, as the temperature of the solution is lowered, the thermal energy of the rotations around the  $\sigma$  bonds connecting methylene groups of the flexible spacer diminishes and eventually becomes lower than the torsional barrier of the particular single bond. At this temperature (ca. 270 K) rotations seem to cease and the

## SCHEME 2



aliphatic chains freeze in a nearly all staggered conformation. This conformation, however, leads to entirely different mutual orientation of the fluorophore dipoles in the odd and even polymers, as shown in Figure 2b. Thus, in the ideal case, the angle formed between two neighboring fluorophores is ca.  $60^\circ$  for the odd polymers and  $0^\circ$  for the even ones. Of course in reality, the angles formed between the fluorophores will not be exactly  $0^\circ$  or  $60^\circ$  for two reasons: first, because the conformation adopted by the aliphatic chain will not be the all staggered, due to the large size of the polymers and the  $-O-C_{12}H_{25}$  side chains attached to the *p*-quinquephenyls, and second, because the absorption and emission dipoles of the fluorophores are not collinear, as we have shown, but instead form an angle of ca.  $10^\circ$ . Additional support for this interpretation comes from the transition temperature at which  $r(ss)_{\text{exp}}$  of the different even polymers shows the sudden increase. Thus, as the aliphatic chain length increases from 8 to 10 to 12 carbon atoms, the transition temperature decreases from ca. 290 to ca. 270 K. This happens because the longer the aliphatic chain is, the higher its flexibility will be and therefore the lower the temperature at which it will adopt the nearly all staggered conformation.

The temperature range of 270–290 K in which the transition of the aliphatic spacers from their all staggered conformation takes place is rather high probably due to the fact that both ends of the aliphatic spacer are immobilized to the rigid segments. It is comparable to the transition named “side chain melting” in hairy-rod polymers in which aliphatic groups are laterally attached onto a rigid polymeric backbone.<sup>24–26</sup> These transitions appear at 300–350 K and are attributed to the increased mobility of the side chains due to the free rotation of the aliphatic carbon–carbon bonds. Also it has been shown that the mobility of the side chains in hairy-rod polymers depends on the topology. Thus in a detailed study of the dynamics of the side chains<sup>27</sup> in such systems, different mobilities were obtained for the aliphatic side groups, with their outer part being more mobile than the units located closer to the grafting points onto the rigid main chain parts. This increased side chain mobility results in some cases in conformational changes of the rigid main polymeric backbone, which is also observed in the temperature range of 300–350 K.<sup>27,28</sup>

The steady-state fluorescence anisotropy  $r(ss)$  is in effect an average, calculable from the fluorescence intensity decay  $I(t)$  and the time dependent anisotropy  $r(t)$ , as expressed by eq 5.<sup>29</sup> Therefore, to relate  $r(ss)_{\text{exp}}$  to the different conformations of

$$r(ss)_{\text{calc}} = \frac{\int_0^\infty I(t)r(t) dt}{\int_0^\infty I(t) dt} \quad (5)$$

these polymers (and the ensuing differences in the mutual orientation of their fluorescence dipoles as shown in Figure 2b) we have calculated  $r(ss)_{\text{calc}}$ , from eq 5, by examining the time evolution of the anisotropy  $r(t)$ , at low temperature, when molecular motions have ceased and only energy transfer contributes to the depolarization of the fluorescence.

**Time-Resolved Fluorescence Anisotropy.** In a decay experiment, after the elimination of the excitation light pulse, the

data are usually expressed as eq 6 where  $I(t)$  is the time dependent quantity measured,  $A$  and  $B$  are constants, and  $T$  is the lifetime of the event studied. For the case of the fluorescence

$$I(t) = A + B \exp\left(-\frac{t}{T}\right) \quad (6)$$

anisotropy,  $I(t) = r(t)$ , i.e., the time dependent fluorescence anisotropy,  $A = r_\infty$ , i.e., the magnitude of  $r(t)$  at very long time,  $B = r_0 - r_\infty$ , and  $T = \Theta$  is the characteristic time scale of the energy transfer. For the case of the fluorescence intensity  $F$ ,  $I(t) = F(t)$ ,  $A = 0$  (the decay is monoexponential), the preexponential factor  $B = 100\% = 1$  and  $T = \tau_f$ . Therefore eq 6 becomes eq 7 for  $F(t)$  and eq 8 for  $r(t)$ .

$$F(t) = \exp\left(-\frac{t}{\tau_f}\right) \quad (7)$$

$$r(t) = r_\infty + (r_0 - r_\infty) \exp\left(-\frac{t}{\Theta}\right) \quad (8)$$

However, we were not able to use direct fitting procedures to the  $r(t)$  data points, because our pulse width ( $\sim 780$  ps) is comparable to the decay times ( $\tau_f \sim 1$  ns) of our samples. Therefore, we used the Impulse Reconvolution Analysis method, which is appropriate for similar situations.<sup>18</sup> According to this method, eq 8 is fitted to the experimental data  $D(t)$ , while in the fitting procedure the program takes into account the impulse response function, which is obtained by fitting to the experimentally derived sum function  $S(t)$ . When to the experimental data of the decay of  $r(t)$ , examples of which are shown in Figure 3, we fitted eq 9, we found the parameters  $\Theta$  and  $r_0$ , listed in

$$D(t) = r(t)S(t) = \left[r_\infty + (r_0 - r_\infty) \exp\left(-\frac{t}{\Theta}\right)\right]S(t) \quad (9)$$

Table 2. Note that these fittings were obtained by using a fixed value for  $r_\infty$ , estimated from the experimental decay of the anisotropy (Figure 3). Substituting then eqs 7 and 8 to eq 5 we found the calculated values of the steady-state fluorescence anisotropy  $r(ss)_{\text{calc}}$ , which are also listed in Table 2, along with the low-temperature experimental values of  $r(ss)_{\text{exp}}$ . It is clear that the  $r(ss)_{\text{exp}}$  and  $r(ss)_{\text{calc}}$  are in very good agreement with each other, for both odd and even polymers.

To further investigate these findings, we have examined the energy migration along a polymeric chain, for fixed orientation  $\theta_{\text{da}}$ , and a constant distance  $R$ , between donor and acceptor fluorophores, as shown schematically in Scheme 2, which depicts the electronic energy hopping between *p*-quinquephenyl moieties.  $M_d$  (donor) is the fluorophore directly excited by the pulse, and  $M_1, M_2, M_3, \dots$  (acceptors) stand for the fluorophores whose excited states are populated via energy transfer from a neighbor excited quinquephenyl moiety,  $\Gamma$  is the intrinsic decay rate ( $1/\tau_f$ ), and  $k_{\text{eet}}$  is the rate constant for energy hopping between adjacent fluorophores. Note the right-left symmetry with respect to the originally excited fluorophore  $M_d$ , which implies that  $k_{\text{eet}}$  is the same all over the chain. When the excitation of the donor is spread among  $i$  acceptors, the overall

fluorescence anisotropy is given by eq 10,

$$r(t) = r_d(t) + \sum r_i(t) \quad (10)$$

where  $r_d(t)$  is the anisotropy of the fluorophore directly excited and  $r_i(t)$  is the anisotropy of the  $i$ th acceptor, both given by eqs 11.

$$r_d(t) = \frac{P_d(t)}{P_d(t) + \sum P_i(t)} r_0$$

$$r_i(t) = \frac{P_i(t)}{P_d(t) + \sum P_i(t)} \frac{1}{2} (3 \cos^2 \theta_{da} - 1) r_0 \quad (11)$$

$P_d(t)$  and  $P_i(t)$  stand for the excitation survival probabilities at time  $t$  following the exciting pulse, with the initial condition  $P_d(0) = 1$  and  $P_i(0) = 0$ , while eqs 12 are the differential equations describing the evolution of these probabilities,

$$\frac{dP_d(t)}{dt} = -2k_{\text{cet}}P_d(t) - \frac{1}{\tau_f}P_d(t) + k_{\text{cet}}(P_1(t) + P_2(t))$$

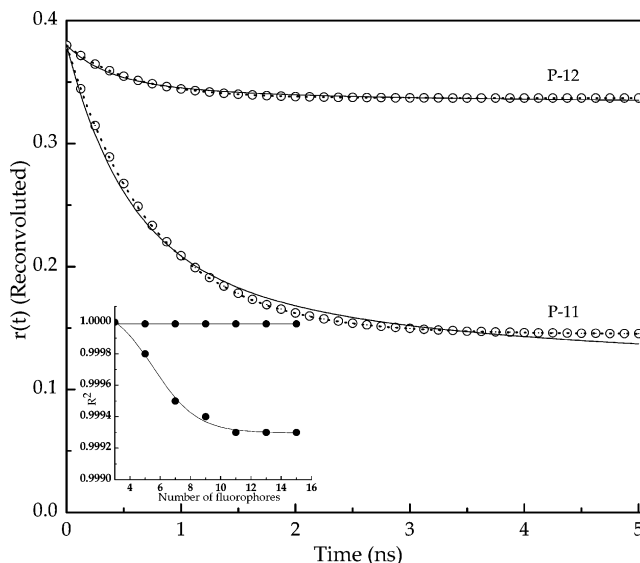
$$\frac{dP_1(t)}{dt} = -2k_{\text{cet}}P_1(t) - \frac{1}{\tau_f}P_1(t) + k_{\text{cet}}(P_d(t) + P_3(t))$$

$$\frac{dP_2(t)}{dt} = -2k_{\text{cet}}P_2(t) - \frac{1}{\tau_f}P_2(t) + k_{\text{cet}}(P_d(t) + P_4(t)) \quad (12)$$

and in general for  $i \geq 3$ , eqs 12 become eq 12'

$$\frac{dP_i(t)}{dt} = -2k_{\text{cet}}P_i(t) - \frac{1}{\tau_f}P_i(t) + k_{\text{cet}}(P_{i-2}(t) + P_{i+2}(t)) \quad (12')$$

Note that for  $\theta_{da} = 0$ , i.e., the case of a parallel donor–acceptor system,  $r(t) = r_d(t)$ , since the fluorescence anisotropy is not affected by the energy transfer. According to eqs 3, 4, 10, 11, and 12', the values of  $r(t)$ , apart from its dependence on  $r_0$ , also depend on  $i$ , the number of acceptors to which the excitation is transferred, on  $R_0$ , and on the angles  $\theta_{da}$ ,  $\theta_d$ , and  $\theta_a$ . However, simulations of eq 10 have shown that  $r(t)$  is not sensitive to the angles  $\theta_d$  and  $\theta_a$ , as long as these are compatible with  $\theta_{da}$  (see Figure 2a) and also are such that the value of  $\kappa^2$  remains within the allowed limits, viz.,  $0 < \kappa^2 < 4$ . We next fitted eq 10 (after making the appropriate substitution of eqs 11 and 12') to the “true” decay data, i.e., the convoluted decay of anisotropy, which is derived according to the evaluated parameters from the Impulse Reconvolution Analysis method (Table 2). The fits were performed by keeping  $\theta_a$  and  $\theta_d$  constant ( $\theta_d = \theta_a = 30^\circ$  for the odd and  $\theta_d = \theta_a = 10^\circ$  for the even) and assuming initially only two acceptors, i.e., 1 chromophore on either side of  $\mathbf{M}_d$ , while  $\theta_{da}$  and  $R$  were left free. In both the even and odd polymers, the fits for only two acceptors, shown in Figure 4 (dotted lines), were very good, with  $R^2 = 0.99999$  in either case. However, since in reality the excitation spreads among many more than three fluorophores along the length of each polymeric unit, we considered more than two acceptors of the excitation energy, viz., four to fourteen. We found that, while in the case of the even polymers the fitting of the experimental points to the appropriately modified eq 10 was very acceptable ( $R^2 > 0.9999$ ) for  $i$  up to 15, in the case of the odd polymers the fittings were deteriorating as  $i$  was increased,  $R^2 \sim 0.999$  for  $i = 15$  (see the inset in Figure 4). The values of  $\theta_{da}$  and  $R$ , in the good fittings of the even polymers for  $i = 15$ , were  $\theta_{da} = 17.1^\circ$  and



**Figure 4.** Comparison between the reconvoluted experimental and theoretical fluorescence anisotropy decays vs time, calculated for  $i = 3$  monomers involved in the energy exchange process, i.e., the originally excited chromophore and the two adjacent chromophores (dotted lines) and for  $i = 15$  monomers (solid lines). Inset:  $R^2$  vs  $i$ , note the deterioration of the fitting for odd polymers as  $i$  increases.

$R = 25.2 \text{ \AA}$ , respectively. These findings suggest that in the even polymers, below 260 K, the aliphatic chains adopt a conformation very close to the nearly all staggered one. Contrarily, in the odd polymers a number of low-energy conformations around the lowest all staggered seems to exist, in which the angle  $\chi_{da}$  varies. However, it must be emphasized that although in the odd polymers we do not have the order observed in the even polymers, we do not have a totally random orientation of the acceptor dipoles either, because in such case the magnitude of  $r_\infty$  should be equal to  $r_0/i$ , therefore even for  $i = 10$ ,  $r_\infty$  should be equal to ca. 0.04, whereas Figures 3 and 4 show that  $r_\infty$  at  $T = 100 \text{ K}$  is quite larger, viz., ca. 0.13–0.14.

It is obvious that the values of the parameters  $\theta_{da}$  and  $R$  obtained from these fittings for the case of the even polymers are in good agreement with the values of the corresponding structure of Figure 2b. Indeed, the angle  $\theta_{da}$  is theoretically equal to  $0^\circ$  while from the fit it turns out to be equal to ca.  $17^\circ$ . However, in view of the fact that the real situation deviates from the perfect all staggered conformation and that the absorption-emission dipoles of the *p*-quinquephenyl fluorophore are not collinear but instead form an angle of  $10^\circ$ , the angle of  $17^\circ$  found is not unreasonable. The case of  $R$ , i.e., the distance between the donor and acceptor dipoles, obtained from the fit, viz.,  $R = 25.2 \text{ \AA}$ , needs more elaboration. Thus, in these polymers the length of the *p*-quinquephenyl fluorophore is larger than the distance between two successive fluorophores along the polymeric chain, e.g. in the case of **P-12** the former is  $20.15 \text{ \AA}$  and the latter  $18.9 \text{ \AA}$  (see Figure 2b). In this situation it is not quite clear how the donor–acceptor dipole distance ( $R$ ) should be measured—from the end points of the *p*-quinquephenyls or between some other point along the fluorophore dipole, e.g., the midpoint. In any case, the value of  $R = 25.2 \text{ \AA}$ , obtained from the fit for **P-12**, is clearly compatible with the dimensions of the polymers, as shown in Figure 2b.

To confirm that this odd–even effect is a property of the polymer, independent of the solvent, we studied additional solvents, viz., chloroform, dichloromethane, tetrahydrofuran, and toluene, which although they do not form glasses, they freeze

below the temperature at which the effect occurs. In all these cases the effect was observed and demonstrated practically the same behavior as with 2-MeTHF. Finally, thin films of these polymers exhibit the odd–even effect.

### Conclusions

This work has clearly demonstrated, for the first time, the so-called odd–even effect in dilute solutions of polymers. The effect was observed by means of steady state and time resolved fluorescence anisotropy, which has proved to be very appropriate for such studies. **We have attributed this effect to the different mutual orientation of the fluorophore dipoles, in** the odd and even polymers, when the temperature is lowered and the flexible aliphatic chains adopt the nearly all staggered, lowest energy conformation. However, although in the case of even polymers the all staggered conformation predominates at the low temperatures, and in the odd polymers it appears that there are other low energy conformations which contribute to the fluorescence anisotropy.

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