

Spectroscopy of macrocyclic poly (9,9-dimethyl-2-vinylfluorene) as an artificial light harvester

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Abstract. The photophysical properties of macrocyclic poly (9,9-dimethyl-2-vinylfluorene) have been characterized by steady state fluorescence and ultrafast spectroscopy. Ultrafast transient absorption anisotropy studies show that energy migration occurs on a picosecond time scale.

Three-dimensional crystal structures for the light harvesting antenna complexes of photosynthetic bacteria have recently been resolved [1]. This has led to a more profound understanding of how nature harvests sunlight in an efficient fashion. The antenna complex (LH2) is highly symmetric and the deployment of chromophores is cyclic. It is therefore of interest whether this architecture is important for the very rapid and efficient energy transfer - excitation hopping times at room temperature of ~ 100 fs have been reported [2]. In our investigations, the ring-like structure of LH2 is mimicked in novel two-dimensional macrocyclic polymers, which have recently been synthesized [3]. Such poly-vinyl aromatic polymers can be prepared with 10 – 50 chromophore groups (here the chromophore is 9,9 dimethylfluorene) that are pendent to the polymer backbone. In this report, the steady state and time-resolved spectroscopic properties of the macrocyclic polymers are compared with their linear analogs.

A 1kHz Ti:S regenerative amplifier producing 100 fs pulses centered at 800 nm pumps an optical parametric amplifier (OPA). Sum-frequency generation of the OPA signal with residual 800 nm pump followed by frequency doubling is used to produce pump pulses at a wavelength of 300 nm. The variably delayed probe beam is generated from a separate portion of the 800 nm fundamental. The pump-probe instrument response function is ~ 170 fs as determined by difference frequency cross-correlation measurements. Both the pump and probe pulses are focused into a 0.5 mm path length CaF_2 flow cell containing poly(9,9-dimethyl-2-vinylfluorene), linear or cyclic, dissolved in cyclohexane. The probe is polarized at 45° with respect to the pump in order that parallel and perpendicular transient absorption components may be simultaneously detected. This is achieved by separating the parallel and perpendicular probe fields by a Wollaston prism after the sample and employing two detection photodiodes, which are in turn connected to lock-in amplifiers referenced to a mechanical chopper in the pump path. The two time-resolved signals obtained are then used to calculate the anisotropy, which is fit with a bi-exponential decay function. Absorption and steady-state fluorescence measurements for fluorene, linear and cyclic poly (9,9-dimethyl-2-

vinylfluorene) with different degrees of polymerization (DP_n) have also been recorded. All experiments were performed at room temperature.

The absorption spectra of both the linear and cyclic polymers have very similar characteristics. As seen in *Figure 1a*, the spectra for both systems overlay and, other than a small blue shift, are in fact virtually identical to the chromophore 9,9-dimethylfluorene free in solution. This indicates that in the ground state there is minimal electronic interaction between adjacent chromophore molecules as expected for a non-conjugated polymer. The fluorescence spectra for both polymers, however, reveal an enhancement in emission in the cyclic polymers opposed to their linear analogs (*Fig. 1b*).

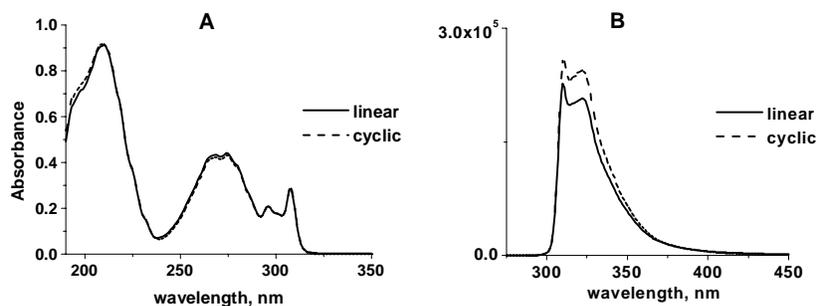


Fig. 1. Absorption and fluorescence spectra of macrocyclic polymer and its linear analog

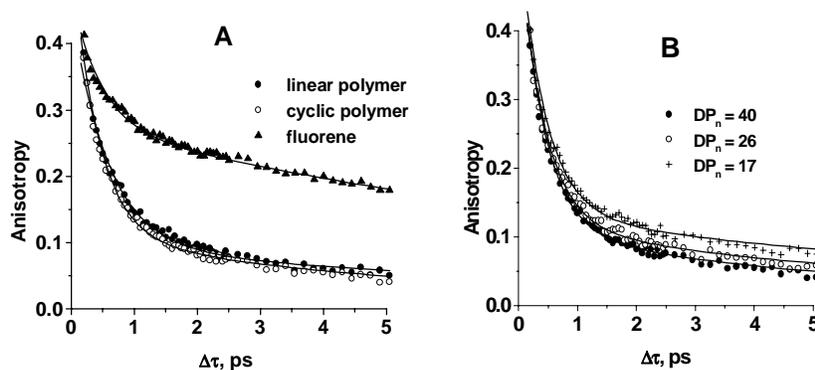


Fig. 2. (a) Anisotropy decay for fluorine monomer and linear and cyclic polymers; (b) as a function of DP_n in macrocyclic polymers.

Figure 2 shows the femtosecond transient absorption anisotropy data for isolated fluorene and the linear and macrocyclic forms of poly (9,9-dimethyl-2-vinylfluorene) in cyclohexane. The dependence of the anisotropy decay with size of the macrocyclic polymer (expressed as its degree of polymerization, DP_n) is

also shown. For fluorene, which represents the free chromophore in solution, an initial anisotropy of 0.4 is observed, indicating that the excited state absorption transition dipole is parallel to the pumped ground state transition dipole. The anisotropy decay is characterized in terms of 2 time constants, 460 fs and 11 ps. The longer time constant corresponds to the rotational reorientation time of the free chromophore, and this value is consistent with other aromatic compounds with similar structure (*e.g.*, anthracene, 8 ps) [4]. At times longer than 20 ps, the residual anisotropy for fluorene is 0.01, which implies that the distribution of the transition dipole moment is almost completely random.

With the chromophore pendent to the polymer backbone, we no longer expect to observe rotational reorientation by tumbling on the reported timescales. The anisotropy decay is substantially altered for the polymers, however the short decay component recovered from the fits, is essentially the same, ~420 fs for both linear and cyclic polymer. We speculate that the early anisotropy decay phase for the polymer system is associated with librations of pendent chromophores on the polymer backbone[5]. The values for the longer decay component differ slightly between the linear ($\tau=7.2$ ps) and cyclic ($\tau=5.0$ ps) form of the polymer. As rotational diffusion of the entire polymer takes place on much longer timescales, the decay of the anisotropy must be interpreted in terms of energy transfer between adjacent chromophore groups along the polymer backbone. When the size of the macrocycle is varied, the observed trend is that the rate of energy transfer decreases with a decrease in the degree of polymerization. This is possibly due to increasing strain in the smaller rings. The strain may cause steric repulsion between pendent chromophores in smaller rings, which will in turn make the inter-chromophore distance larger resulting in a slower rate of energy transfer. We note that there is a residual anisotropy observed that increases with decreasing ring size. This observation suggests that the transition dipoles in the smaller rings are closer to coplanar than in larger ones. The rates for energy transfer implied by our results agree well with predictions based on Forster's Theory. However, the extent of depolarization in a single hop of the excitation depends intimately on the angle between adjacent chromophore molecules. Therefore, to thoroughly extract information from the datasets on the rate and dispersion of energy migration in these chromophore architectures, energy transfer simulations based on an ensemble of polymer structures are required and such calculations are in progress.

References

1. G. McDermott, S. M. Prince, A. A. Freer, A. M. Hawthornthwaite-Lawless, M. Z. Papiz, R. J. Cogdell, N. W. Isaacs, *Nature* **374**, 517 (1995).
2. R. Jimenez, S. N. Dikshit, S. E. Bradforth, G.R. Fleming, *J. Phys. Chem.* **100**, 6825 (1996).
3. Y. Gan, D. Dong and T. E. Hogen-Esch, *J. Am. Chem. Soc.* **122**, 2130 (2000).
4. G. S. Jas, Y. Wang, S. W. Pauls, C. K. Johnson and K. Kuczera, *J. Chem. Phys.* **107**, 8800 (1997).
5. A. T. Sengupta, M. D. Fayer, *J. Phys. Chem.* **96**, 8619 (1992).