Site-Addressable Polymer Dynamics Probed with 2D-IR

Laura M. Kiefer, John T. King and Kevin J. Kubarych

Department of Chemistry, University of Michigan, 930 N. University Ave., Ann Arbor, MI 48109, USA
kubarych@umich.edu

Abstract: A polymer consisting of transition metal carbonyl sites enables dynamical readout of ultrafast structural fluctuations in dilute, concentrated, and thin film conditions. 2D-IR spectroscopy and coarse grained simulations reveal distinct dynamics of the ends.
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1. Introduction: Polymer Dynamics

There have been few studies of the ultrafast structural dynamics of polymer chains that, unlike biomolecules such as peptides and DNA, are essentially structureless and are well suited for comparison to basic theories of polymer dynamics. Since ultrafast spectroscopy provides excellent temporal resolution to reveal molecular motions, we seek to develop spectroscopically site-addressable polymeric systems with essentially homogeneous chemical composition in order to compare location-specific dynamical measurements with simulation and theory. For example, reptation is a key aspect of polymer dynamics that relates directly to the molecular rheology (i.e. friction and transport properties), where an entangled polymer chain is considered to move "forward and back" within a tube defined by the constraints imposed by neighboring chains [1]. Motion within the tube is primarily Brownian diffusion in reduced dimensionality. The chain dynamics themselves become important as the ends meet obstacles, where further motion is linked to the timescale of chain end fluctuations.

Using a recently developed method of polymerizing transition metal containing complexes, we have performed two-dimensional infrared (2D-IR) spectroscopy on a short 8-unit long chain of poly(cyclopentadienylcarbonyl-diphenylphosphinobutanoyliron) (PFpP) (Fig. 1) [2]. Because the $CpFe(CO)_2$ terminus and the main $CpFe(CO)$ chain are spectroscopically distinct, we are able to address simultaneously the dynamics of the end chain separately from the inner-chain sites. We leverage the very strong nonlinear signals associated with metal-carbonyl vibrations to follow the dynamics at concentrations ranging from dilute solution (THF) to a spin-cast thin film. The primary experimental method is ultrafast 2D-IR spectroscopy, where we track the site-specific differences in the time-correlation function of the frequency fluctuations ($\langle\delta\omega(0)\delta\omega(t)\rangle$, FFCF) of the strong vibrations of $Fe(CO)$ (1900 cm^{-1}) and $Fe(CO)_2$ (1945 and 2000 cm^{-1}).

The 8-mer polymer is too large for DFT, but we are able to estimate the optimized geometry using semi-empirical methods (AM1/Gaussian 09) in order to employ simple polymer models for elucidating trends in chain dynamics at the level of individual sites. To investigate general dynamical behavior of coarse grained models of the polymer, we used a simple model with Lennard-Jones sites linked by harmonic springs, while incorporating varying
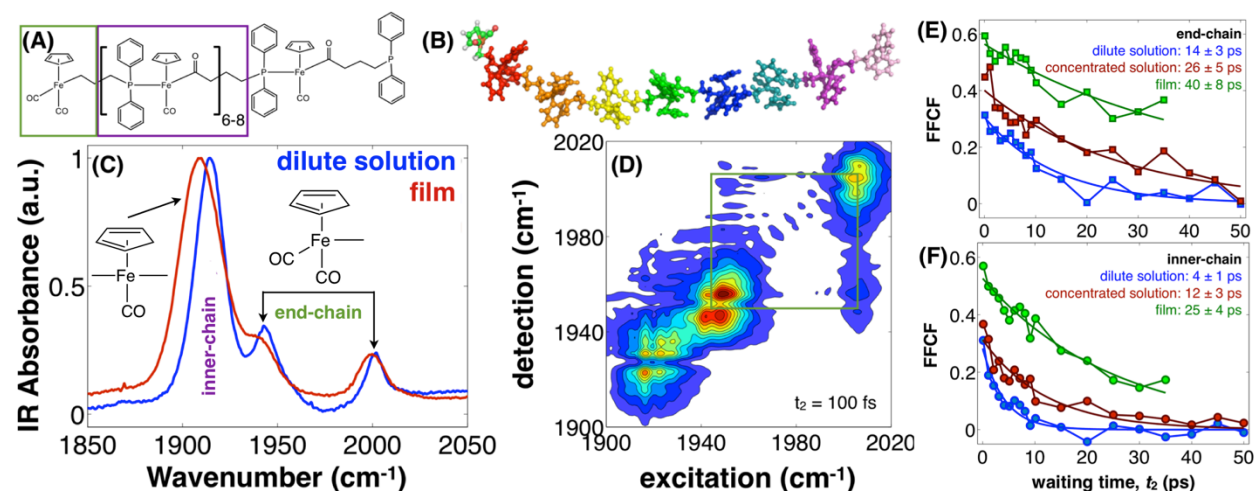

Fig. 1. (A) Chemical structure of PFpP and AM1 semi-empirically optimized geometry (B). Note the $CpFe(CO)_2$ terminus on the left. (C) FTIR spectra of the 8-mer polymer in THF solution and in solvent-free film. (D) Early waiting time (t_2 = 100 fs) 2D-IR rephasing spectrum of the dilute sample showing reabsorption and some scattering. (E) FFCFs of the end-chain 2000 cm^{-1} dicarbonyl band for the three sample conditions, and (F) the inner-chain 1900 cm^{-1} band. In all three conditions, the end chain fluctuates more slowly than the inner chain sites.

degrees of harmonic bond angle potentials. The main goal of the resulting Langevin dynamics simulations (LAMMPS) is to identify signatures of chain dynamics, particularly for the relatively short polymer we studied. Most common analytical polymer models treat either very large polymers or more highly averaged properties than the site-level information we require. Remarkably, over a wide range of parameters the simulations tend to reproduce the essential site-specific fluctuations measured using 2D-IR, as discussed below.

2. Experimental Results: Spectral Diffusion is Slower at the Ends

Solutions of $(PFpP)_8$ in THF were studied with 2D-IR spectroscopy. Due to the relatively high linear absorption of even the dilute samples, there is some distortion in the 2D lineshapes. Since absorption affects the rephasing and non-rephasing pathways equally, our method of employing the "inhomogeneity index," as opposed to graphical analysis of the absorptive peak shapes, avoids complications due to the distortions [3]. Cross peaks are observed only between the two bands of the dicarbonyl terminal site at 1945 and 2000 cm^{-1}. We find no evidence for vibrational energy transfer from the dicarbonyl to the monocarbonyl inner-chain sites.

Two features of the data are immediately apparent. Within each sample, the end chain spectral diffusion is markedly slower than the inner-chain. For example, in the dilute solution, the FFCF of the end chain decays with an exponential time constant of 14±3 ps, whereas the inner-chain sites decay with a faster 4±1 ps time constant. Due to the homopolymer nature of the system, all of the inner-chain sites are essentially identical, precluding more fine grained site-specific probing within the inner-chain. Nevertheless, as mentioned in the introduction, the dynamics of the chain end is key to understanding key aspects of polymer transport.

The second clear finding is that increasing the concentration slows the spectral diffusion significantly for both the end and inner chain locations. The chain-end spectral diffusion slows threefold to 40±8 ps, while the inner-chain slows sixfold to 25±4 ps when the polymers are cast into a thin film. That the chain end slows to a lesser degree than the inner chain is consistent with an excluded volume effect: the end becomes more constrained within the cavity formed by the neighboring polymers.

3. Simulation Results: Chain Ends Typically Fluctuate Slower

Polymer structures are commonly characterized by nondynamical quantities such as their mean end-to-end distances or their radii of gyration. We introduce a measure of site-specific structural fluctuations by computing the instantaneous distance Δr_k from each site k to the center of mass of the chain. We extract dynamics by computing the site-specific time-correlation functions $\langle \Delta r_k(0)\Delta r_k(t)\rangle$. The correlation functions are well fit to biexponentials (not shown), yielding two time constants that typically differ by an order of magnitude. Though the details depend on the strength of the bond-angle potential energy term, a general trend emerges from a set of simulations. The average time constant computed by integrating the normalized correlation functions shows that the ends of the chain relax

Fig. 2. Coarse grained simulation showing the relative average time constant for the fitted decay of the $\langle \Delta r_k(0)\Delta r_k(t)\rangle$ correlation function.

slower than do the inner chain sites (**Fig. 2**). The ratio of the end to inner chain time constants is roughly a factor of three, which is consistent with the experimental results, though at this point the agreement may be fortuitous. Nevertheless, the simple model supports the experimental finding that the ends relax more slowly than do the inner chain sites. Future model studies will incorporate crowding in concentrated conditions, in order to confirm the reduced relative slowdown for the concentrated solution and the film.
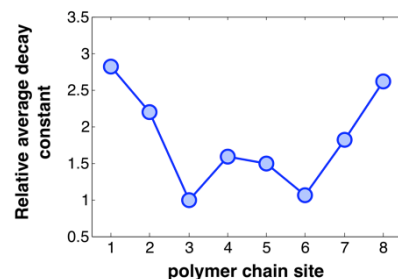
4. Conclusions and Outlook

2D-IR spectroscopy has provided many insights into the structure and dynamics of biomolecule dynamics, and here we show that the method is also able to shed new insight into the heterogeneous dynamics of more general polymer chains. The experimental methodology permits investigations of polymers in dilute solution as well as in solvent-free films, and coupling the experiments with simple but informative coarse grained simulations enables a new dynamical picture of site-level fluctuations.

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