



Femtosecond fluorescence dynamics and molecular interactions in a water-soluble nonlinear optical polymeric dye

O. Varnavski, T. Goodson III *

Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

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Abstract

The excited state dynamics of a water-soluble polymeric dye poly(S-119) was investigated using femtosecond time-resolved fluorescence upconversion. Multi-exponential relaxation of fluorescence was observed for poly(S-119) in picosecond and sub-picosecond time ranges. The azo-chromophore of the functionalized polymeric dye Sunset Yellow was used as a model compound for detailed investigations of intermolecular interactions. Excited state decay of this azo-dye can be described by a two-exponential decay law with time-constants of ~ 0.48 ps and 1 ps. Fluorescence anisotropy decay was investigated for both systems. The difference in excited state dynamics between the polymeric dye and the azo-chromophore is explained in terms of inter-molecular interactions resulting in intra-chain aggregate formation. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

It is now accepted that organic macromolecular materials have potential applications in nonlinear optics (NLO), optical switching, photo-refractive effects, optical limiters, and light emitting diodes [1–4]. The increased activity of research into the properties of optical macromolecular materials has been motivated by considerations of solvent–solute effects [5], guest–host properties [6], thin film optical properties [7,8], and macromolecular interactions in the liquid

and condensed phases [9–12]. These considerations have inspired new directions for nonlinear optical and electro-active macromolecules particularly in the area of biological applications of NLO effects. The use of large and de-localized nonlinear effects of non-toxic polymers embedded in biological hosts provides new opportunities for cell probing and for precise ablation of the biological tissue [13]. Indeed, molecular interactions upon excitation of the NLO chromophores attached to the polymer become important in regard to these applications as they may determine the dimensions (scale) of the nonlinear effect in the biological host. Thus, it is important that the intermolecular interactions in polymeric dyes be understood in order to design better NLO polymeric systems for biological applications.

* Corresponding author. Fax: +1-313-577-8822; e-mail: tgoodson@chem.wayne.edu

To gain further insight into the role of intermolecular interactions in polymeric dyes, it is important to analyze the nature of elementary excitation and relaxation dynamics in the ultra-fast time scale regime [9,10]. In this Letter we investigate the azo-polymeric dye S-119 and the azo-chromophore Sunset Yellow. Spectroscopically, the azo-benzenes are characterized by a low-energy (n to π^*) state with a weak lower energy absorption band [14]. Time-resolved studies have suggested that trans-to-cis and cis-to-trans isomerizations proceed extremely fast (2.5 ps [15] and 170 fs [16], respectively). From similar ultra-fast measurements two mechanisms of this fast decay in azo-benzene chromophores have been proposed. The fast nuclear motion may proceed by either a rotation around the N–N bond resulting in a change in torsion angle or by an in-plane inversion with reorientation located to a single nitrogen center [15].

While these findings are indeed firm for simple azo-benzene structures, the ultra-fast dynamics of substituted and more complex systems is not well understood. The applications of azo-benzene containing polymers in optical data storage are closely associated with a fast isomerization process [7,17]. This effect in polymeric films is strongly related to the number of isomerization cycles per second (isomerization rate). The photoisomerization rate is dependent on spatial restrictions [18] and on aggregation processes caused by intermolecular interactions [19]. Azo-chromophore aggregation can inhibit the rate of photoisomerization and lead to a decrease of optical storage capabilities [20]. If the detailed information about the fast dynamics of each cycle is obtained then new information regarding the efficiency (or capability) of an optical data storage process can be obtained. However, there have been no reports on ultra-fast photoisomerization dynamics in polymers with pendant azo-chromophores. Using fluorescence upconversion we have investigated the fast dynamics of the polymeric azo-dye S-119. The dynamics of the azo-chromophore Sunset Yellow was also investigated for a comparison. This is the first report of ultra-fast fluorescence measurements that gives complementary information to previously reported pump–probe experiments aimed at clarifying the character of isomerization process in azo-chromophores [15,21,22]. The purpose of these in-

vestigations was to probe intermolecular interactions in the polymeric system that also resulted in an enhancement of the NLO effect observed in femtosecond light fields [13].

2. Experimental

The polymeric dye S-119 and the chromophore Sunset Yellow (1-*p*-sulfophenylazo-2-naphthol-6-sulfonic acid disodium salt) were purchased from the Sigma Chemical. Their structures are shown in Fig. 1A. Solutions were made with 3 mg of the polymeric dye S-199 in 5 ml of water or with appropriate amount of SY resulting in equal molar concentration of the chromophore group. For experiments testing concentrated solutions of SY, concentration of about 55 times greater was used. Solutions were filtered with 0.1 μm filters to remove impurities. Time-resolved fluorescence of S-119 and SY was studied by using the femtosecond upconversion spectroscopy technique [23]. The sample solution was excited with frequency-doubled light from a mode-locked Ti-sapphire laser (Tsunami, Spectra Physics). This produces pulses of approximately 100 fs duration at a wavelength of 395 nm. Our upconversion apparatus also consists of the basic unit of the FOG-100 system (CDP). The polarization of the excitation beam for the anisotropy measurements was controlled with a Berek compensator. The sample cuvette was of 1 mm thick and was held in a rotating holder to avoid possible photo-degradation and other accumulative effects. The horizontally polarized fluorescence emitted from the sample was upconverted in a nonlinear crystal of β -barium borate using a pump beam at 790 nm that was first passed through a variable delay line. This system acts as an optical gate and enables the fluorescence to be resolved temporally with a time resolution of about 200 fs (pump-excitation 790/395 nm cross correlation function had a FWHM of 190 fs). Spectral resolution was achieved by dispersing the upconverted light in a monochromator and detecting it by using a photo-multiplier tube (Hamamatsu R1527P). The average excitation power was kept at a level below 3 mW. In this excitation intensity regime the fluorescence dynamics was found to be independent of the excitation intensity for all investigated solutions. The fluorescence decay curves

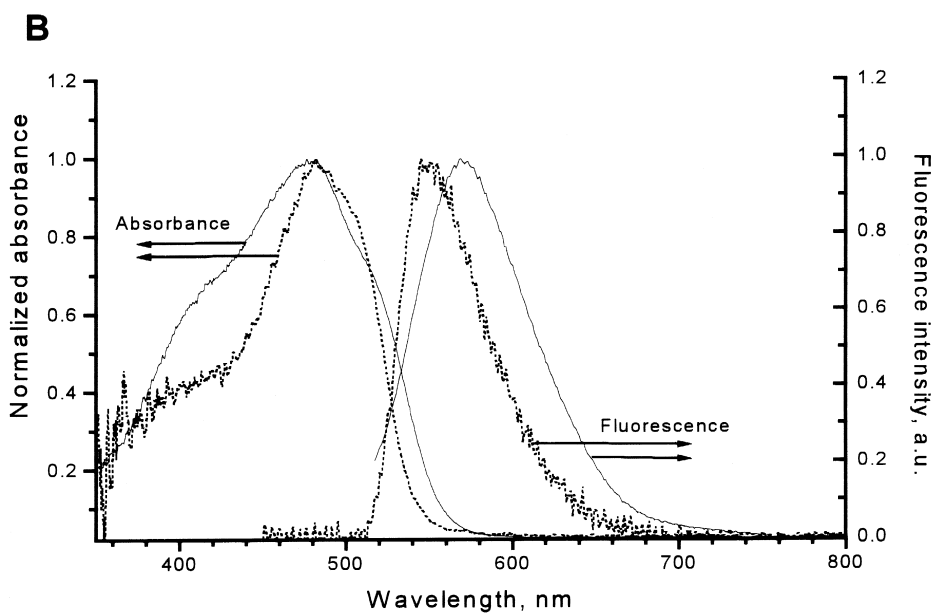
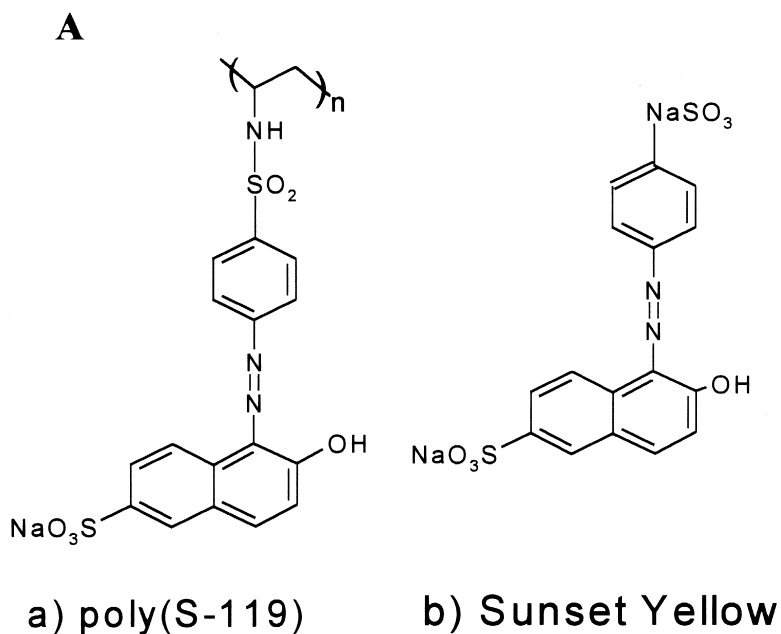


Fig. 1. (A) The structure of water-soluble polymer poly(S-119) (a) and functional group Sunset Yellow (b) used in the study. (B) Absorption and fluorescence spectra of poly(S-119) and Sunset Yellow in aqueous solution. The noisier spectra are for Sunset Yellow.

were fitted to the result of convolution of the instrument response function with an exponential model to minimize the reduced χ^2 value [24]. The minimum value was obtained by the Marquardt non-linear least

squares method. The quality of the fit was monitored by values of the reduced χ^2 as well as by inspection of the residuals and autocorrelation function. UV-visible absorption spectra were recorded with a

Hewlett-Packard 8452A diode array spectrophotometer and the fluorescence spectra were measured with a Shimadzu RF-1501 spectrofluorophotometer.

3. Results and discussion

The principal absorbing (and emitting) species in our polymeric dyes S-119 is an azo-dye. As stated above, the optical properties of simple representative azo-dyes such as azo-benzene have been studied extensively in the literature [14–16,25]. Specifically it has been found that the S_0 – S_1 transition for these dyes is a weak ($n\pi^*$)-transition, while the strong allowed transition ($\pi\pi^*$) is an S_0 – S_2 transition [25,26]. However, for azo-benzene derivatives the position of the ($\pi\pi^*$)-transition depends on particular substitution, while the position of the ($n\pi^*$)-transition is practically unchanged by substitution in aromatic azo-systems [14,26]. These trends may lead to overlapping or even reordering of the electronic transitions [21,22]. Indeed, for our systems S-119 and SY, the UV-visible absorption spectra show that the lowest transition at about 480 nm is a ($\pi\pi^*$)-transition. The UV-visible absorption and fluorescence spectra of water solutions of S119 and Sunset

Yellow (SY) are shown in Fig. 1B. The broadening of the absorption peaks in S119 compared to SY as well as the larger Stokes shift for S119 indicates the interaction of chromophore groups in the polymer backbone or between each other.

As can be seen from the structures in Fig. 1A the S-119 possesses many of the functionalities necessary for large electronic NLO effects, due to the relatively large degree of conjugation and the existence of dipolar groups on the side chains. Indeed we observed high nonlinear refraction and two-photon absorption of S-119 at different wavelengths. The detailed investigation of nonlinear properties of water-soluble non-toxic polymeric dyes is given elsewhere [13]. The nonlinear refraction coefficient of S-119 at 800 nm was found to be $n_1 = 2.3 \times 10^{-5} \text{ cm}^2/\text{GW}$ for the solution of 6.7 mg/mL concentration. Here we present the close-aperture Z-scan results of S119 and SY (shown in Fig. 2). The nonlinear refraction of the material can be easily estimated from peak-to-valley distance of Z-scan-curve [27]. It is clearly seen from Fig. 2 that the polymeric dye S-119 exhibits higher nonlinear refraction as compared to the isolated chromophore group SY at the same molar concentration. This enhancement of nonlinear refraction in the polymer dye (S-119) can be

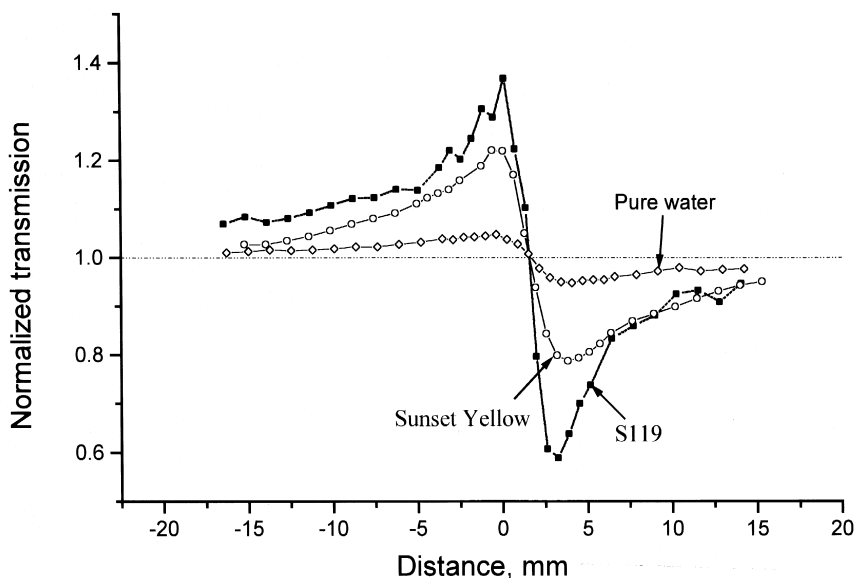


Fig. 2. Comparison picture of close-aperture Z-scans for S-119, Sunset Yellow and water at 800 nm. Peak irradiance at focal waist: $8.6 \text{ GW}/\text{cm}^2$.

suggestively related to the interaction between chromophore groups on the polymer backbone leading to a formation of new states with enhanced transition dipole moments.

In order to gain further insight into the role of different functional groups of the polymer S-119 we probed the excitation energy pathways and the interactions between different functional groups with ultra-fast fluorescence dynamics measurements. The fluorescence decay of S-119 was found to be non-exponential (the emission dynamics can only be satisfactory fit by a three-exponential decay law) and emission wavelength dependent. In Fig. 3 the decay of fluorescence of S-119 is depicted for different emission wavelengths. The decay can be roughly characterized it by an initial $1/e$ decay time of about 2.2 ps at 580 nm and the observed decay becomes slower as the spectral detection window is shifted towards lower energies. Non-exponential character of the decay functions along with the emission wavelength dependence may indicate the presence of several simultaneously emitting states. It is well known that short relaxation times lead to very low quantum efficiencies of integrated fluorescence and the poly-

meric dye S-119 has been referred to as a non-fluorescent polymeric dye for this reason [28].

In contrast to the S-119 the emission dynamics of SY has been found to be much closer to mono-exponential and independent of the detection wavelength (shown in Fig. 4, SY1). The corresponding decay can be fitted with two-exponential decay function with very short time constants of 0.48 ps 1 ps, and relative amplitudes of 0.67 and 0.33, respectively. The ultra-fast in-plane inversion was suggestively associated with a $S_1(n-\pi^*)$ -transition in the azo-benzene chromophore while the relatively slow (~ 15 ps) large-scale rotation around the $-N=N$ -bond occurs following $\pi-\pi^*$ excitation [15]. However, the recent reports [21,22] showed that the excitation into the lowest-lying electronic transition of azo-benzene derivative results in an ultra-fast (< 1 ps) isomerization process regardless of the nature of the lowest-lying transition ($n-\pi^*$ or $\pi-\pi^*$). Our fluorescence decay results following a $\pi-\pi^*$ excitation of SY support these findings.

The π -electron conjugation in the side chain azo-benzene chromophore in S-119 is disrupted at the SO_2 group (Fig. 1a). However, the excitation may be

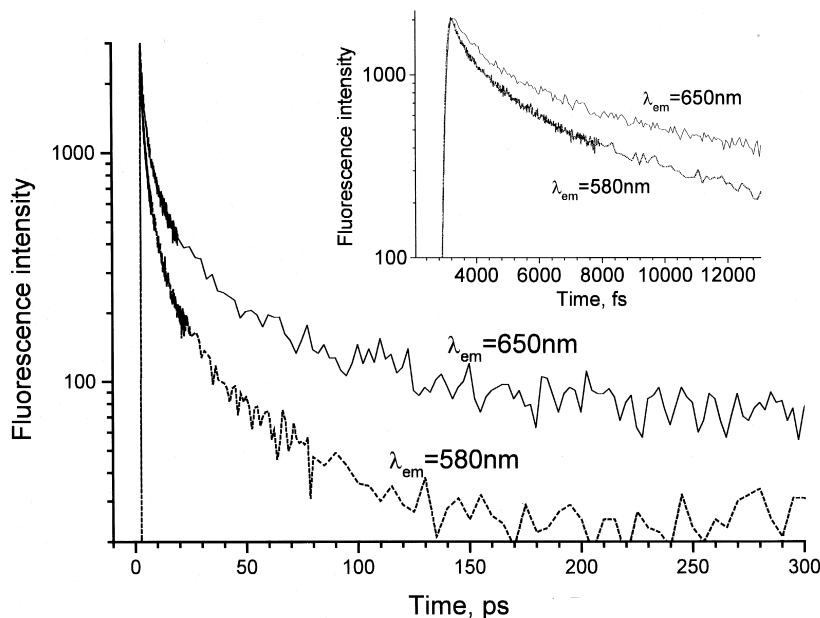


Fig. 3. Fluorescence decay of poly(S-119) in water for different emission wavelengths, when excited at 395 nm. Inset: the short time-scale decay.

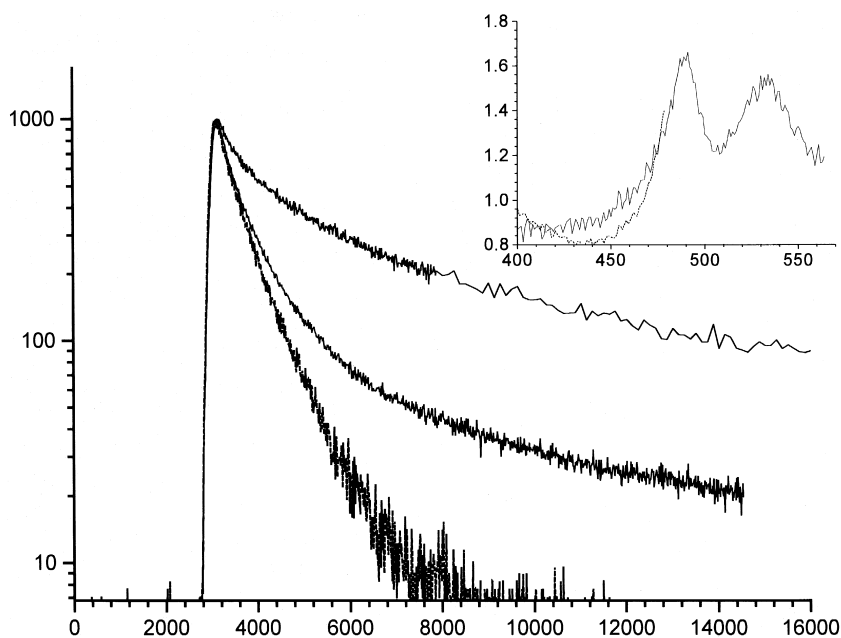


Fig. 4. Fluorescence dynamics of poly(S-119) (S119) and Sunset Yellow (SY1,SY2) in water at two different concentrations: SY1, 1.38×10^{-3} mol/L, SY2, 7.58×10^{-2} mol/L. Excitation wavelength is 395 nm. Inset: Excitation spectra of the fluorescence at 580 nm for poly(S-119) (S119) and Sunset Yellow (SY) at low concentration of 1.38×10^{-3} mol/L.

delocalized over several chromophores due to dipole–dipole or exchange interaction. These delocalized excitonic states are actually the states of intra-molecular aggregates. The shift of the fluorescence maximum of the S-119 polymeric system to the red in comparison to that observed for the chromophore SY, as well as the appearance of long-lived components in the fluorescence dynamics, may indicate such chromophore aggregation either in the excited state (excimers) or in the ground state.

To gain better insight into the mechanism responsible for the lifetime elongation in case of S-119 we measured the fluorescence dynamics of concentrated solution of SY (Fig. 4, SY2). The appearance of long-lived component as compared to the diluted solution of SY1 is clearly seen. Formation of the molecular aggregates with relatively long-lived excited state in the concentrated solution is the obvious reason for this effect. This result supports the idea of formation of the somewhat similar intra-chain aggregates in S-119. Note that the molar concentration of chromophore group in S-119 was the same as for diluted solution of SY1. On the other hand the

distance between two adjacent azo-chromophores in S-119 was estimated to be approximately 3–5 Å. This implies that *inter-chain* aggregate formation should be ruled out in our case. Indeed, the fluorescence dynamics was found to be independent of concentration in case of S-119. In order to clarify whether the above aggregation in S-119 is formed in the excited state (excimer) or ground state we compared the fluorescence excitation spectra of S-119 and SY1. The result shown in the inset to Fig. 4 clearly demonstrates an appearance of additional excitation band at 532 nm in case of S-119 as compared with SY1. This result indicates the formation of the intra-chain aggregate in the ground state. We fitted the decay curves of SY1, SY2, S119 to a three exponential function (separately, not using a global fit). The results of the fit for SY2 and S119 show approximately the same pair of short time-constants as those for SY. The relative amplitude of the third long-lived component increases from almost zero for SY to 0.28 for S119.

A parallel-type aggregation (H-aggregates) associated with the blue-shifted absorption peak has been

suggested for some azo-benzene chromophores [19, 20]. However, in case of S119 we observed an additional excitation peak shifted to the red from the monomer (SY) absorption peak, which is characteristic of a J-aggregation [29–31]. An important parameter related to the increase of nonlinear refraction of S-119 as compared to SY (Fig. 2) is the exciton delocalization length in the intra-chain aggregate. In general, the delocalization length can be estimated from either superradiant enhancement of radiative lifetimes of aggregates as compared to the monomer [29] or from the exciton ‘motion narrowing’ of the spectral line upon aggregation [30]. As it was noted above the fluorescence quantum yield of S-119 is very low and the measured fluorescence fast decay is predominantly non-radiative. The same is true for the monomer SY. In these conditions it is impossible to measure the change in radiative lifetime upon aggregation with reasonable accuracy. An obvious line narrowing upon aggregation was neither observed for fluorescence or for the absorption lines. This may indicate the small delocalization length (few monomers) and a broad distribution of physical sizes in aggregates as well. The spectral shift upon aggregation was used to estimate the delocalization length in polymer bound J-aggregates [31]. In our case this shift was estimated to be approximately 1600 cm^{-1} . Unfortunately, we have no second reference point for the spectral shift for very long aggregates which is necessary for evaluation of delocalization length as in case of the system investigated by Horng [31]. However, the spectral shift can be used for a rough estimate of the interaction strength between two adjacent chromophores in the S-119 polymeric dye. It can scale from 800 cm^{-1} for infinite aggregates to 1600 cm^{-1} for a dimer provided that the interaction with the environment (solvent, backbone) is the same for both monomer and aggregate.

It is worth noting that there is an absence of a rise-time feature in the fluorescence dynamics of S-119. Even for emission wavelengths as far to the red as 680 nm, no detectable rise-time was observed. This indicates either extremely fast ($< 200\text{ fs}$ time resolution of the setup) energy transfer from initially excited individual chromophores to the intra-chain aggregates or direct excitation of the aggregates (in spite of the excitation wavelength being rather far apart from the excitation peak of these species (532

nm)). Although the relatively high fluorescence anisotropy value for the emission of aggregated species (0.205, see below) strongly supports direct excitation of the aggregates, the possibility of fast energy transfer between orientationally correlated individual chromophores and aggregates can not be completely excluded at this point.

The elongation of the fluorescence lifetime of S119 indicates the decrease of the effective isomerization rate. The analysis of the decay curves (Fig. 4) shows a decrease in the relative contribution of fast components more than by a factor 4.5 going from SY to S119. It is well known that the exciton delocalization (aggregation) hinders conformational movements. We consider this effect to be the main reason of the appearance of a relatively long-lived fluorescence of S119. This is justified by changes in the steady state spectra as well as by the similar fluorescence dynamics for concentrated SY2. However, the distance between adjacent chromophores in S119 is about 3–5 Å, which gives a volume comparable to that required for unperturbed isomerization movements and may inhibit the isomerization process [18]. These spatial constraints may also contribute to the complex fluorescence dynamics observed for S119.

We have estimated the fluorescence anisotropy fast dynamics of both S-119 and SY by measuring the fluorescence polarized perpendicular and parallel to the polarization of excitation light. Fluorescence anisotropy $r(t)$ is defined as

$$r(t) = (I_{\parallel} - GI_{\perp}) / (I_{\parallel} + 2GI_{\perp})$$

where $I_{\parallel}(t)$ and $I_{\perp}(t)$ are the fluorescence intensities parallel and perpendicular to the excitation polarization, respectively. Factor G accounts for the difference in sensitivities for the detection of emission in the perpendicular and parallel-polarized configurations. We obtained this factor from our test measurements of fast rotational diffusion of perylene in solution [32]. The fluorescence anisotropy decay for S-119 in comparison with that for SY on a time scale of SY lifetime is shown in Fig. 5a. The isotropic (the normal relaxation) fluorescence decay of SY is also shown for comparison. It is seen that within experimental error the fluorescence anisotropy remains constant for decay times as long as twice the fluorescence lifetime of Sunset Yellow. This is in accor-

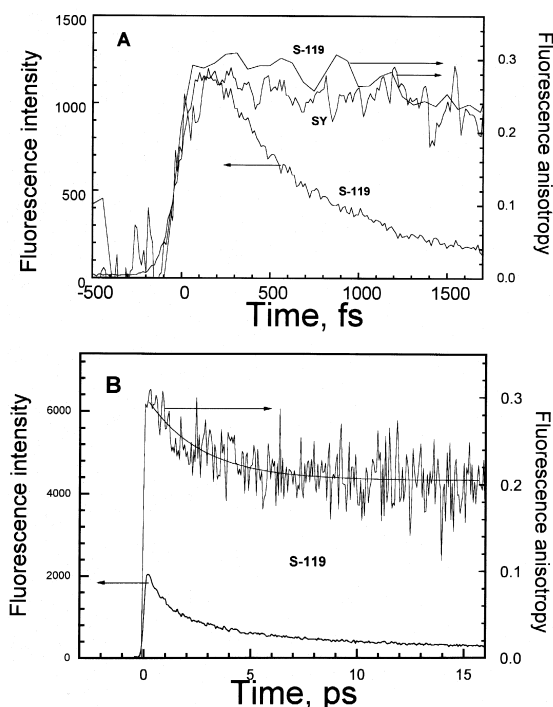


Fig. 5. Time-resolved fluorescence anisotropy decays of poly(S-119) and Sunset Yellow. Excitation wavelength, 395 nm; emission wavelength, 580 nm. (A) Short-time scale. The isotropic fluorescence decay of SY is given for comparison. (B) Fluorescence anisotropy decay of poly(S-119) on the longer time scale. The best fit line for fluorescence anisotropy is shown. The isotropic fluorescence decay of S-119 is also given for comparison.

dance with the homogeneous character of the SY emission line demonstrated by the emission wavelength independent isotropic decay noted above. The result of the fluorescence anisotropy decay of S-119 on the longer time scale of 20 ps is shown in Fig. 5b. It is apparent that there is a few picosecond time-scale decay of fluorescence anisotropy to a non-zero value, which is independent of time out to about 20 ps. This fast anisotropy decay component can not be associated with the molecular motion as the hydrodynamic radii for this polymer is so large that the anisotropy relaxation time due to rotational diffusion is in the sub-microsecond time range. Comparing the anisotropy decay with the isotropic fluorescence decay of S-119 (also depicted on Fig. 5b) one can see that the anisotropy decay time is about the same as the fast decay component of the isotropic fluorescence dynamics of S-119. We suggest that the fluorescence

anisotropy dynamics shown in Fig. 5b is simultaneously related to the polarized emission of the intra-chain aggregates and the individual chromophores in the polymer environment. As this takes place, the time-dependent component of the fluorescence anisotropy shown in Fig. 5b can be associated with the decay of the individual chromophores (non-aggregated). At the same time the time-independent contribution of the anisotropy can be assigned to the polarized emission of relatively long-lived intra-chain aggregates.

4. Conclusions

We have measured the intrinsic ultra-fast polarized fluorescence dynamics of a water-soluble polymeric azo-dye poly(S-119). To probe the interactions between different functional groups of the polymeric dye the fluorescence dynamics of an azo-chromophore Sunset Yellow was also investigated. Specifically, we found that the fluorescence decay of S-119 is emission wavelength dependent and multi-exponential with an initial $1/e$ decay time of about 2.2 ps at 580 nm. At the same time the fluorescence of SY decayed faster with time-constants of ~ 0.48 ps and 1 ps. The lifetime elongation in the case of S-119 indicates the decrease of the effective rate of the photo-isomerization process. A detailed comparative study of the fast fluorescence dynamics and the steady state fluorescence excitation spectra of the poly(S119) and Sunset Yellow showed that the ground state intra-chain aggregate is formed in the polymer. The ultra-fast fluorescence decay of SY was assigned to an isomerization process. The complex dynamics of S-119 can be explained in terms of inter-chromophore interactions resulting in intra-chain aggregate formation, and also by the possible contribution of short-range inhomogeneous spatial effects. The important consequence of the reported aggregate formation is a 2-fold increase in the nonlinear refractive index of S-119 as compared to SY.

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