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Solvation Dynamics of Chromophores in Polyethers

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Steady-state and time-resolved optical techniques are employed to measure the solvation static and dynamics of large probe molecules in small polyethers. In ethylene glycol dimethyl ethers ($n = 2$, 3, and 4) we find that the solvation dynamics span from ∼50 fs to more than 100 ps. Three major time components can be resolved. The short time is bimodal with an ultrafast Gaussian component <70 fs followed by a ∼2 ps component. The second component of 10−20 ps depends on the polymer size and is attributed to segmental motion. The long component of >100 ps is ascribed to cooperative motion of the polymer matrix.

Introduction

It has been known for many years that polymers consisting of polar groups are capable of direct interaction with various salts. These ion−polymer complex properties have been used extensively in organometallic chemistry.[1−4] With the growing concerns for future energy generation and conservation that will be environmental friendly, a rapid development in research relating to these “polymer electrolytes” have been made.[5−11] The fundamental feature that distinguishes a polymer electrolyte from other conductive systems that are currently in use is the net ionic motion in polymer electrolytes that takes place without long-range displacement of the solvent. Ion transport in polymer electrolytes is considered to take place by a combination of ion motion coupled to the local motion of polymer segments and inter- and intrapolymer transition between ion coordinating sites.[6] To act as a successful polymer host, a polymer should generally have at least three essential characteristics:[10] (1) atoms or group of atoms with sufficient electron donor power to form coordinate bonds with cations; (2) low energy barrier to bond rotation so that segmental motion of the polymer chain, which is crucial to ionic transport, can take place readily; and (3) suitable distance between coordinating centers in order to enable the formation of multiple intrapolymer ion bonds, which appears to be important.

Although a number of materials fulfill these criteria, none of them have the qualifications that poly(ethylene oxide) has as a host polymer. Poly(ethylene oxide), to date, has been the most widely studied polymer in this field.[7,10,12] The range of salts that may dissolved in this polymer is large; however, attention has focused principally on a small group of lithium and sodium salts that form polymer electrolytes of potential commercial interest. In general, the efficiency of the polymer electrolyte depends on the segmental movement of the polymer host, and a large study has been done about the long time motion of this polymer by electrochemical methods.[13,14] That is the reason we found it of interest to study the dynamics of small polymers acting as a solvent, using optical spectroscopy techniques.

In our previous works we have studied the salt effect on solvation dynamics of large probe dye molecules in a wide range of organic solvents.[15] We use probe molecules to measure the relaxation time of the solvation energy after a change in the probe charge distribution due to electronic excitation. The solvation dynamics are measured from the time-dependent Stokes shift of the probe fluorescence. In this study we will compare our results to those of other groups that studied the dynamics of tetrapolyether molecules, using ultrasonic techniques[16,17] and molecular dynamics simulations.[18] In those simulations they found that the intrasegmental molecular relaxation times for ethylene oxide dimer and tetramer are 10 and 25 ps, respectively. These motions of the polymer contribute to ion transport in polymer electrolyte.[10]

We have measured the time-resolved fluorescence of a probe molecule, coumarin 153 (C153), in tetraethylene glycol dimethyl ether (PEG4), in the temperature range of 215−293 K, using a time-correlated single photon counting technique. For the short time range (less than 10 ps), an ultrafast femtosecond spectroscopy technique[19,20] is utilized. For these experiments we used polymethine dyes as solvation dynamics probes. We also used the ultrafast techniques for the measurements of the relaxation of shorter polyether chains, triglyme and diglyme, that we report here.

Experimental Section

Time-resolved fluorescence was detected by time-correlated single-photon counting (TCSPC). As an excitation source we used a CW mode-locked Nd−YAG-pumped dye laser (Coherent Nd−YAG Antares and a 702 dye laser) providing short pulses [2 ps at full width at half-maximum (fwhm)] at 1 MHz repetition rate. The (TCSPC) detection system is based on a Hamamatsu 3809 photomultiplier, Tennelec 864 TAC, and 454 discriminator. A personal computer was used as a multichannel analyzer and for data storage and processing. Measurements were taken at 5 ns full scale (5 ps/channel). The instrument response function, fwhm, is 50 ps.

Tetraethylene glycol dimethyl ether or tetraglyme (PEG4), triglyme (PEG3), and diglyme (PEG2) were purchased from Sigma, coumarin 153 (C153) was from Eastman Kodak, 3,3-diethylthiatricarbocyanine (DTTC) was purchased at Koch-Light, and rhodamine 800 was purchased from Exciton. The materials were used without further purification.

Ultrafast Techniques. For times shorter than ∼20 ps we used ultrashort laser pulses and four wave mixing techniques. The optical setup is based on Heterodyne Optical Kerr Effect (HOKE). A passively CW mode locked Ti−sapphire laser (Coherent Mira 900F) pumped by an argon ion laser (Coherent Innova 310) is used to produce a 76 MHz train of short pulses

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with 70−120 fs fwhm tunable in the optical range of 720−800 nm. The laser output beam of 6 nJ/pulse is split into pump and probe beams with an intensity ratio of 3:1, respectively. In the time-resolved resonance HOKE experiment, the laser-induced anisotropy created by the resonant absorption of the pump pulse photons is probed by a variably delayed, weak polarized probe pulse. The change in the polarization state of the probe beam is detected by the transmission through a crossed polarizer pair of the probe beam as a function of the time delay between the pump and the probe pulses. To amplify the optical Kerr signal and to avoid complexity due to the quadratic nature of the signal, we use heterodyne methods in the signal detection.[21]

The local oscillator was in phase with the signal. In such a case the signal intensity measures the imaginary part of the third-order nonlinear polarization, i.e., the sample dichroism. The sample was measured in a rotating cell to avoid thermal contribution to the OKE signal. Unlike the nonresonant OKE measurement, which is used to measure the dynamics of the liquids,[22] the resonance measurements provide the solvation dynamics of the probe molecules in solution.

Results and Discussion

Steady State. The steady-state emission spectrum of coumarin 153 shows a red shift with respect to increasing polarity of the solvents. We found that the magnitude of the shift is better described by the π^* polarity scale[23] than by the $E_T(30)$ scale.[24] We used π^* values of known solvents from ref 23. Figure 1 shows the excitation and emission spectra of coumarin 153 in a series of organic solvents from the nonpolar one, cyclohexane, to the polar solvent, PEG4. As one can see from panels a and b of Figure 1, the red shift is larger for the fluorescence spectra than for the excitation spectra, which is in agreement with what we expected from coumarin 153 as a positive solvatochromic compound. From the plot of the emission maxima vs π^* values (Figure 2) we were able to estimate the polarity of the solvents that we used. The π^* values of PEG4, PEG3, and PEG2 as we found are 0.69, 0.65, and 0.64,[23] respectively. The polarity slightly decreases with the reduction in the molecular weight of the polymers. The polarity, π^* values, of the polyethers are similar to that of acetic acid.

Time-Resolved Fluorescence at Different Temperatures. Figure 3 shows the normalized spectral response function, $C(t)$, obtained for coumarin 153 in PEG4 at 243 K. $C(t)$ was calculated from time-resolved spectra over the range of 460−640 nm, measured at 10 nm intervals, according to

$$C(t) = \frac{\nu(t) - \nu(\infty)}{\nu(0) - \nu(\infty)} \qquad (1)$$

where $\nu(t)$, $\nu(\infty)$, and $\nu(0)$ are the fluorescence frequencies, at the band maximum, at times t, ∞, and zero, respectively. To obtain those values we followed the procedure described by Maroncelli and co-workers.[25,26] This procedure is time-consuming in both measurements and data analysis. Barbara and co-workers developed, and used, an alternative time-saving procedure for measuring the spectral response function that requires only a single emission transient and certain photophysical data on the probe.[27−29] The central assumption of the method is that the dynamical solvent effects that are responsible for the time dependence of the fluorescence spectrum (both shape and radiative rate) are due to a single, generalized solvent coordinate such as the solvent polarization. For coumarin153 the characteristic wavelength was found to be at 470 nm.[30] Figure 3 shows also the time-resolved fluorescence decay curve at 470 nm. One can see that the two lines are almost overlapping and therefore the single characteristic wavelength method, i.e., the time-resolved emission of coumarin 153 at 470 nm, can be used to measure the solvation correlation function.

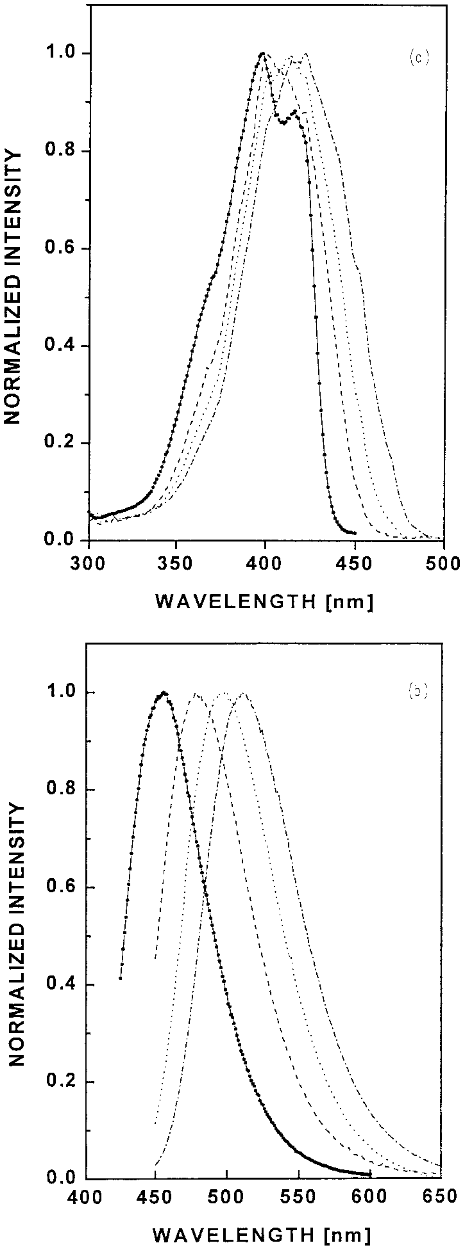

Figure 1. Steady-state spectra of coumarin 153 in different organic solvents: (●) cyclohexane, (- - -) diethyl ether, (···) butyl acetate, and (-·-) PEG4. (a) Absorption spectra; (b) emission spectra.

Figure 4a shows the time-resolved fluorescence decay curves of coumarin 153 in PEG4 measured at 470 nm, in the temperature range of 215−283 K (the freezing point of PEG4 is 243 K). As we see in Figure 4a, the amplitude of the fast component increases as the temperature decreases. We used a sum of three or four exponents for the fit of the fluorescence decay curves and the parameters are shown in Table 1. The average solvent relaxation time, $\langle\tau\rangle$, was calculated according to[31]

$$\langle\tau\rangle \equiv \int_0^\infty \Big(\sum_i a_i e^{-t/\tau_i}\Big)\, dt \qquad (2)$$

As one can see in Table 1, the shortest time component becomes faster as the temperature increases and its contribution

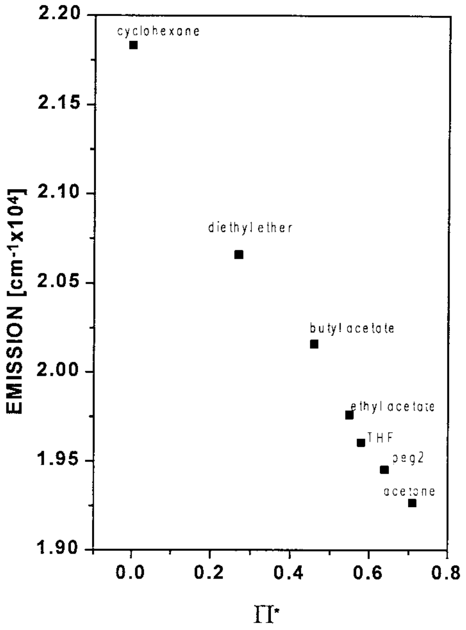

Figure 2. Emission maxima of coumarin 153 vs π values in different organic solvents.

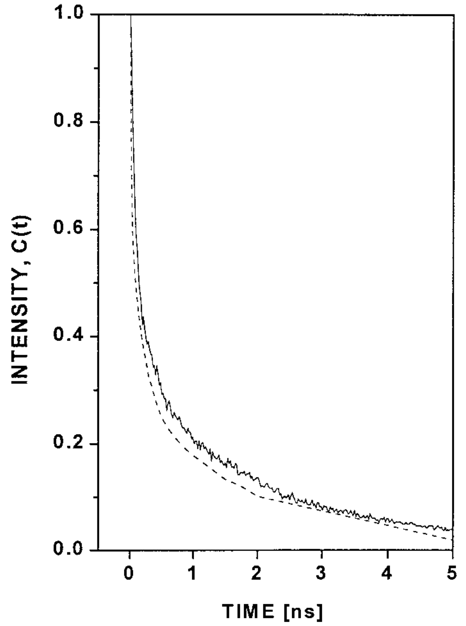

Figure 3. Coumarin 153 in PEG4 at 243 K. (- - -) Solvation correlation function, $C(t)$; (—), and time-resolved fluorescence decay curve at 470 nm.

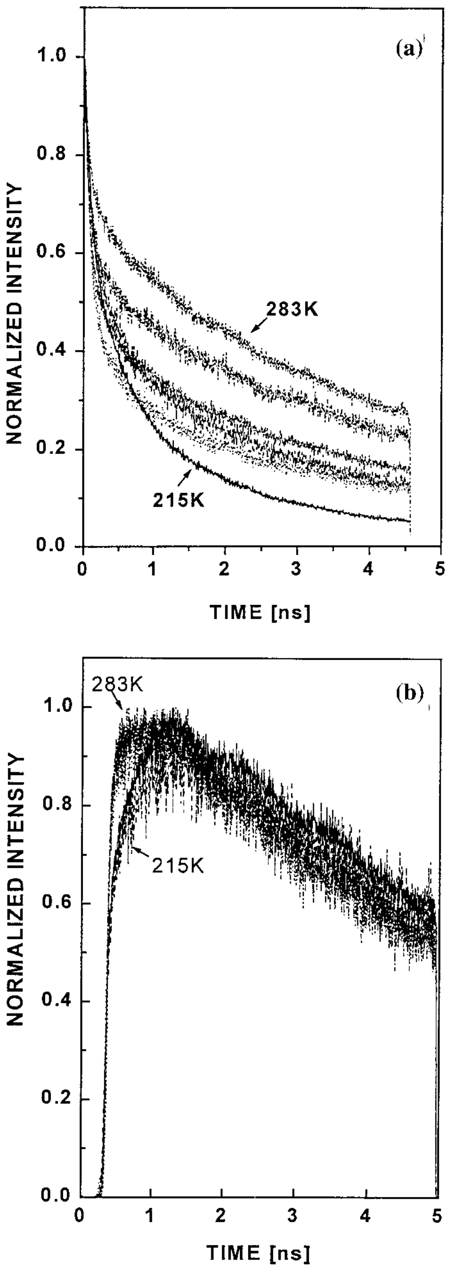

Figure 4. Time-resolved fluorescence decay curves of coumarin 153 in PEG4 at different temperatures, (a) at $\lambda_{\mathrm{fl}} = 470$ nm and (b) at $\lambda_{\mathrm{fl}} = 640$ nm.

to the solvation energy is ~70%. This component is about 10 ps at 283 K and 130 ps just above the freezing point at 243 K. The longer time component has similar temperature dependence as the first one. The decay time changes from 140 to 1150 ps in the temperature range 283−243 K, respectively. Its amplitude is about 30% of the total solvation energy.

We also measured the solvation rate at 215 K. This temperature is 30 °C below the freezing point. We fit the data using four exponents. The average relaxation time increases to 3000 ps. In the solid phase, the polymer motions are partially hindered and the relaxation times are much longer than in the liquid phase.

Figure 5 shows a plot of the average relaxation times versus inverse temperature. From the Arrhenius plot (Figure 5) we obtained an activation energy, E_a, of 7.2 kcal mol^{-1} for the average solvation relaxation time of PEG4 in the temperature range of 215−283 K. Surprisingly, the average relaxation time below the freezing point (215 K) fits well to the Arrhenius plot shown in Figure 5. This interesting observation that solvation occurs also in solids, on time scales shorter than the radiative lifetime, was also found for coumarin 153 in tetraalkylammonium salts.[32] We also found that the activation energies calculated separately for both the fast and the slow relaxation times are similar, i.e., ~7 kcal mol^{-1}. Wang et al.[16] studied the dynamics of tetraethylene glycol by measuring its Brillouin scattering as a function of temperature and obtained the activation energy as 3.85 kcal mol^{-1}. The difference in those values is probably due to structural variance in the polyethylene molecules. In our experiments we used PEG that ends with −OCH, groups, and the polymer used by Wang had −OH end groups.

Short Time Measurements with Series of PEGs. We have used a CW mode locked Ti−sapphire laser with 70 fs pulses,

TABLE 1: Fitting Parameters of the Time-Resolved Fluorescence Data, to a Sum of Three or Four Exponentials, for Coumarin 153 in PEG4 at Different Temperatures[a]

temp [K]	τ_1 (ps) [a_1 (%)]	τ_2 (ps) [a_2 (%)]	τ_3 (ps) [a_3 (%)]	τ_4 (ps) [a_4 (%)]	τ_f (ps) [a_f (%)]	$\langle\tau\rangle$ (ps)
283	10 [54.1]	140 [18.9]			5300 [27]	44
273	25 [55.3]	180 [18.4]			5300 [26.3]	64
263	40 [59.3]	260 [18.7]			5300 [22]	93
253	64 [68.2]	650 [16.7]			6000 [15.1]	179
243	130 [61.2]	1150 [18.9]			6000 [19.9]	371
215	60 [40.7]	220 [25]	900 [25]	30 000[b] [9.3]	6000	3094

[a] τ_i = relaxation times, τ_f = fluorescence lifetime, a_i = amplitudes, and $\langle\tau\rangle$ = average relaxation time (eq 1). [b] This long component was estimated from the longest fluorescence decay component according to $1/\tau = (1/\tau_4)\ (1/\tau_f)$, where τ is the decay time of the fluorescence tail.

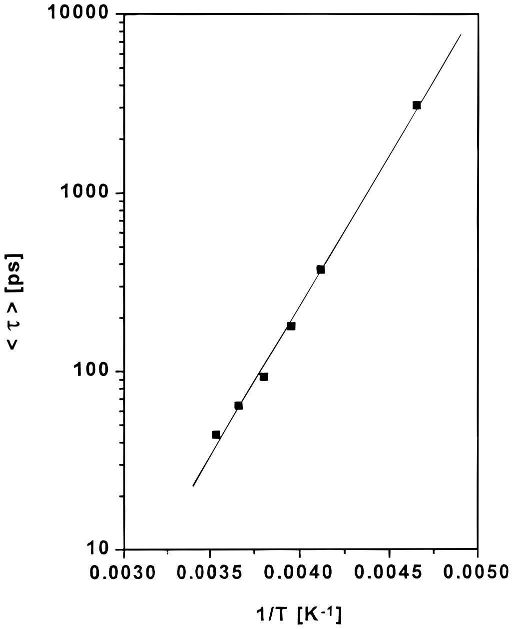

Figure 5. Arrhenius plot of average relaxation times of coumarin 153 in PEG4.

tunable in the range of 720−800 nm, to conduct short time measurements of the solvation dynamics. The experimental technique, Heterodyne Optical Kerr Effect (HOKE), allows us good signal/noise ratio at the ultrafast time range. We measured a series of three polyethers with increasing molecular weight, PEG2, PEG3, and PEG4, using a polymethine probe, 3,3′-diethylthiatricarbocyanine (DTTC). The transient nonlinear optical response depends on the relations between the intramolecular chromophore relaxation and solvation dynamics. Numerous experiments[26,33−35] show that the Franck−Condon molecular state achieved by an optical excitation relaxes very fast and the relaxed intramolecular spectrum forms within 0.1 ps. Therefore, we shall consider the intramolecular relaxation to take place within the pump pulse duration. Such a picture corresponds to a rather universal dynamical behavior of large polar chromophores in polar solvents, which may be represented by four well-separated time scales:[35] an intramolecular vibrational component and intermolecular relaxation which consists of an ultrafast (∼100 fs), 1∼4 ps, and 10∼100 ps decay components. In these experiments we were able to observe quantum beats in the OKE signal. The short time high-resolution HOKE signals of DTTC in the above polyether solvents (Figure 6a) were fitted by an exponential decay and a model of an optically active non- Markovian oscillator (NMO) with exponential decaying memory function (for more details see refs 20 and 36), which account for the quantum beats relaxation. Use of such a model may be explained as follows. The Markovian (Brownian oscillator) description of the dynamic system relaxation (a molecular vibration) is correct only for times that are much longer than the correlation time of the bath. If one assumes that the beat attenuation is related to a solute−solvent interaction, then both the beat attenuation time and the correlation time of the bath (solvent) τ_s will be of the same order, since τ_s is of the order of the solvation relaxation time. In our specific case the beat attenuation is completed within 1 ps. The solvent relaxation span from ∼50 fs to ∼100 ps and

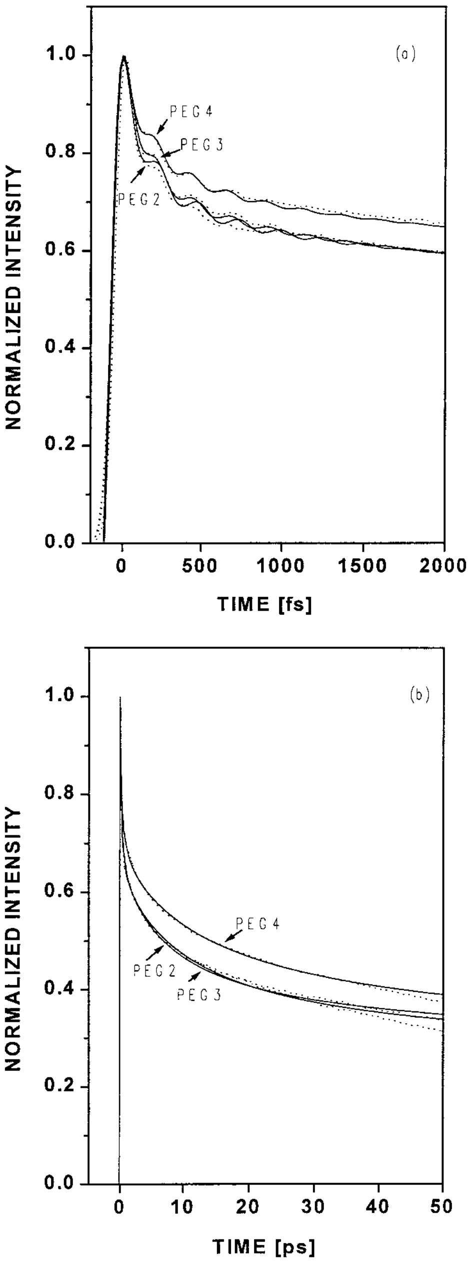

Figure 6. Optical Kerr signals of DTTC in a series of polyethers, using HOKE technique. The dots are the experimental data and the solid lines are the fits.

hence the solvation process is incomplete during the beat attenuation. To describe such an effect, one can use a correlation function, which corresponds to the NMO with an exponential memory function. Although there were not any significant changes among the different polyether solvents in the oscillation's parameters, it is worth mentioning that the memory damping coefficients are similar to those we found for the same probe in alcohols.[20] The non-Markovian behavior is also pointed out by Wang et al.,[37] who measured the Brillouin scattering of polyethylenes of increasing molecular weights.

The HOKE experimental data at long times (>2 ps) were fitted to two exponents (Figure 6b). Those long time components of the signal are attributed to the diffusional part of the solvation correlation function. The shorter component increases with increasing molecular weight: for PEG2, PEG3, and PEG4, $\tau = 11.8$, 15.4, and 18.2 ps, respectively. In addition we measured, with the HOKE optical setup, a time component of 15 ps for the probe rhodamine 800 in PEG4. These values are in good agreement with the shortest time component measured using time-resolved fluorescence technique, with limited time resolution, for coumarin 153 (see Table 1). Those values are also of the same order of the 20 ps measured and calculated for tetraethylene glycol by Wang et al.[16] and Noudou et al.,[17] using Brillouin scattering. In molecular dynamics simulations,[18] the average relaxation times obtained for the molecules $H(CH_2OCH_2)_nCH_3$, with $n = 2$ and 4 were $\tau = 10.3$ and 25.3 ps, respectively. They relate this component to the segmental motions of the chains through the oxygen bonds, which depends, only slightly, on the molecular weight. The longest component is the same for PEG2 and PEG3 and is equal to ~100 ps, while for PEG4 it is slightly longer, ~111 ps. These slow relaxation times, as we obtained here, are in excellent agreement (consider the different measurement techniques and the different probe molecules) with our results from the time-resolved fluorescence measurements for PEG4 with the probe coumarin 153 (130 ps) and with the results for PEG4 with the probe molecule rhodamine 800 using the HOKE technique (125 ps). This component is related to the cooperative motions of the solvent molecules due to creation and annihilation of the network by fast fluctuations.[17] Since we did not find any major difference between the values of the activation energy for the fast and the slow relaxation times, it is plausible that the segmental motions of the polymer control the slow process.

Summary

In this study we have measured the solvation dynamics of several probe molecules in a series of polyethers. We have used several time-resolved optical techniques resolving solvation dynamics from ~50 fs to ~5 ns.

The following results have been obtained: (a) The solvation dynamic of polyethers is complex and spans over 3 time orders. At the shortest times the solvation dynamics is bimodal and can be described by a Gaussian component with a width shorter than our laser pulse width, followed by a ~2 ps exponential decay. The second time component of 10−20 ps depends on the polymer size; i.e., the longer the polymer, the slower the solvation component. This component is attributed to the polymer intramolecular segmental motion. The longest solvation component is 10 times slower, i.e., ~100 ps, and is almost insensitive to the polymer molecular weight. This component we attribute to the cooperative motion of the polymer molecules within the polymeric matrix.

The solvation data are in accord with both the ultrasonic data[16,17,37],and the molecular dynamics simulations findings,[18] which show that segmental motions of the polymer chain account for the observed dynamics.

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