

Ultrafast Dynamics of Styrene Microemulsions, Polystyrene Nanolatexes, and Structural Analogues of Polystyrene

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The ultrafast optically heterodyne-detected optical-Kerr-effect is used to compare the dynamics of styrene neat and in dodecane solution with those of styrene dispersed as the oil phase in a oil-in-water microemulsion. The dynamics in the microemulsion are similar to those of the neat liquid, both on the ultrafast and picosecond time scales, but there is also evidence for additional inhomogeneous broadening in the microemulsion. The styrene in the microemulsion was photopolymerized to yield isolated latex particles. The effect of polymerization on the ultrafast dynamics is dramatic. The picosecond diffusive response seen for the monomer is suppressed, whereas the ultrafast spectral density shifts to higher frequency in the polymer. Similar dynamics are seen for polystyrene in solution. This behavior is further analyzed through an investigation of the ultrafast dynamics of solutions of toluene, bibenzyl, a polystyrene oligomer, and polystyrene itself. It is concluded that the shift to higher frequency in the spectral density corresponds to the opening of additional intramolecular relaxation pathways in the larger more flexible molecules. It is found that both molecular and intramolecular librational dynamics are sensitive to their environment.

I. Introduction

Microemulsions are thermodynamically stable, single-phase mixtures of two immiscible liquids stabilized by a surfactant. They have been the subject of intense interest for more than two decades because of their great practical value in a range of applications, from oil recovery to drug delivery.¹ The ability of microemulsions to solubilize a diverse range of compounds in nanometer-sized dispersions means that they provide excellent media for chemical reactions.^{1,2} Among the most important of these reactions are those aimed at the production of nanoparticles, which themselves have a variety of applications.¹ In this paper, we extend our previous investigations of the ultrafast dynamics of liquids dispersed in microemulsions³ to the reactive styrene–dodecyltrimethylammonium bromide (DTAB)–water system. The ultrafast method employed is the optically heterodyne-detected optical-Kerr-effect (OHD-OKE), which has been widely employed in high time resolution studies of the dynamics of liquids and their mixtures.^{4–6} Despite the large body of work that exists on the characterization of the microemulsion environment, there are rather few studies of the dynamics of the dispersed phase of such systems,^{3,7–13} and there exist no previous studies on the effects of polymerization on those dynamics.

An area of nanoparticle research that has been particularly fruitful is that of microemulsion polymerization.^{2–14,15} It has been found that, by performing polymerization reactions in the dispersed phase of microemulsions, it is possible to create latex particles with very narrow size distributions and controllable diameters in the range of 10–100 nm.² Furthermore, in contrast to bulk and solution phase polymerization, the confinement of the reacting species in a small volume by the micelles means that microemulsion polymerization yields fast reactions and high molecular weight polymers.¹⁶ The field of microemulsion

polymerization is too vast to summarize here, but a number of review articles have been published.^{2,14,15} Of specific interest here is work on the polymerization of styrene–DTAB–water microemulsions.^{16–18} This system has the advantage of not requiring a co-surfactant, thus minimizing complications arising from partitioning of the co-surfactant between phases. Initiation of the polymerization has been achieved via several pathways. Puig et al.^{16,17} employed thermal activation using either aqueous phase potassium persulfate or oil phase 2,2-azobisisobutyronitrile (AIBN) initiators, whereas Steytler et al.¹⁸ employed photolytic initiation with a 2,2-dimethoxy-2-phenylacetophenone (DMPA) initiator. The latter approach was shown, via small angle neutron scattering (SANS), to produce no increase in the micelle size during polymerization.

The OHD-OKE method used here was developed in its most commonly used form by McMorro, Lotshaw, and co-workers,^{19–29} and has been applied extensively to study the dynamics of liquids.^{4–6} More recently, the technique has been employed to investigate the dynamics of complex fluids such as liquid crystals^{30–32} and sol–gel confined liquids.^{33–36} We have shown that under certain circumstances OHD-OKE can be a useful tool for probing the dispersed phase dynamics of a microemulsion.³ The magnitude of the OHD-OKE signal of any given species scales with the polarizability and the number density of that species. Thus, through careful selection of the dispersed, continuous and surfactant components of a microemulsion system, it can be ensured that the signal from the dispersed phase will dominate the OHD-OKE signal. This approach was used to study the dynamics of CS₂ confined in DTAB–water microemulsions,³ where it was found that the constrained CS₂ exhibited dynamics that were intermediate between those of bulklike CS₂ and those of alkane-solvated CS₂. Here we achieve similar contrast by employing the highly polarizable styrene as the dispersed phase.

The results of this study will be reported in three sections. First a comparison is made between the dynamics of bulk

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styrene, styrene dissolved in dodecane, and styrene dispersed in a DTAB–water microemulsion. Although the ultrafast liquid dynamics of benzene and some of its derivatives have been studied with the OHD-OKE technique,^{22,24,37–42} the dynamics of styrene itself have not been reported. This initial section provides an extension of our work on the CS₂–DTAB–water system, yielding information on the effects on the dynamics of varying the molecular size and shape of the dispersed phase component. The data from the bulk and dodecane-solvated styrene provide useful comparisons to facilitate analysis of the microemulsion data. In the second section, we report the OHD-OKE data for the polymerized microemulsion, in which the ultrafast dynamics of the latex particle will be contrasted with those of the dispersed monomer. The third section presents a study of solutions of model compounds toluene, styrene, bibenzyl (1,2 diphenylethane), an oligomer of polystyrene (–CHPh–CH₂–)₈, and polystyrene itself, in both dodecane and carbon tetrachloride. These measurements provide comparative data on the dynamics of structural analogues of polystyrene and its constitutional repeat units, which shed further light on the origins of changes in the dynamics observed on polymerization.

Although ultrafast studies of the liquid dynamics of a few polymers have been reported,^{43–45} polystyrene is not among them. Bauer et al.⁴⁶ applied depolarized Rayleigh spectroscopy to study polystyrene in 1975 but did not report picosecond or subpicosecond dynamics. The transient grating OKE experiment has been used to study polymer systems including studies of ultrafast dynamics.^{43,44} Of particular relevance here is the study of poly-(2-vinyl naphthalene) in CCl₄ solutions, over a range of temperatures by Sengupta et al.⁴³ The observed temperature dependence of the picosecond dynamics in solution was found to be inconsistent with the predictions of a hydrodynamic model. Thus, these dynamics could not be assigned to rotation of the whole molecule, but instead, these, and faster subpicosecond, dynamics were attributed to librational motion of the naphthalene side groups. Similar conclusions were reached in studies of poly(methylphenylsiloxane) and poly(dimethylsiloxane).⁴⁴ Most recently Shirota and Castner⁴⁵ studied aqueous poly-(acrylamide) solutions using OHD-OKE, observing rotational relaxation involving entire constitutional repeat units of the polymer, rather than simple side-group motions.

II. Experimental Section

The OHD-OKE spectrometer employed in this work has been described in detail elsewhere.³ The monophasic microemulsion region (Windsor IV, WIV) of the styrene–DTAB–H₂O system occurs at similar compositions to that of the CS₂–DTAB–H₂O system (a phase diagram for the styrene system can be found in ref 16). The fraction of styrene present in the microemulsion sample is quite low, so it was once again necessary to use the laser-power normalized, differential detection method originally described by Fourkas et al.^{33,34,47,48} to extract reliable data, especially at longer pump–probe delay times. The ultrafast light source used was a Kerr lens mode-locked titanium sapphire laser (Clark MXR). The operating wavelength was 800 nm, with a repetition rate of 100 MHz. The pulse duration was measured by second-order autocorrelation at the sample position as 45 fs, with a time-bandwidth product of <0.5.

Styrene (Lancaster, 99% purity), DTAB (Lancaster, 97%), dodecane (Lancaster, 99.9%), carbon tetrachloride (BDH, spectroscopic grade), toluene (Sigma, 99.9%), bibenzyl (Aldrich, 99%), polystyrene, and the oligomer (Aldrich) were all used without further purification. The water used as the continuous phase of the microemulsion was filtered via a Millipore filtration

system. All samples were passed through 0.22 μ m filters prior to the OHD-OKE measurement, to remove any dust particles. Samples were allowed to equilibrate at the laboratory temperature (295 \pm 1 K).

The microemulsions studied here were formed in a manner similar to the CS₂–DTAB–H₂O microemulsions described previously,³ though in this case styrene was added dropwise to a 20 wt % solution of DTAB in water. With this quantity of surfactant, the phase boundary between the WIV and biphasic WI regions was determined by titration to lie at 10 wt % styrene. As a result, all further studies were performed on a microemulsion containing 8 wt % styrene (volume fraction of the dispersed phase, ϕ = 0.289, x_{styrene} = 0.018, x_{DTAB} = 0.014), a composition which facilitated a good signal-to-noise ratio but which avoided any complications that may have arisen from proximity to the phase boundary. The microemulsions were characterized using conductivity and viscometry, as previously employed for the CS₂–DTAB–H₂O system.³

Polymerization of the microemulsion was achieved using the method of Steyler et al.¹⁸ The microemulsion was produced as described above except that, prior to inclusion in the microemulsion, the styrene was passed through a column (Scientific Polymer Products DTR-7) to remove the inhibitor and then mixed with 0.021 mol-per-mole of styrene of the DMPA initiator. This quantity was estimated to yield an occupancy level of approximately one molecule of initiator per micelle, based upon an assumed DTAB aggregation number of 50 molecules per micelle as discussed elsewhere.³ The microemulsion was exposed to UV radiation for 2 h, after which time the reaction of the styrene monomer was confirmed by the disappearance of the styrene band at 1083 cm^{–1}, observed by FTIR spectroscopy. Polymerization of the microemulsion was also achieved using thermal activation with potassium persulfate or AIBN initiators. However, the method of Steyler et al.¹⁸ was found to give samples of superior optical quality, being free from the slight bluish tint sometimes observed using other methods. A high optical quality of the sample is an important consideration for the OHD-OKE technique.

III. Results

Conductivity and viscometry measurements were carried out on a 20 wt % solution of DTAB in water, as a function of increasing weight % of styrene, up to the phase boundary of the single phase microemulsion. Similar trends in viscosity and conductivity were observed for styrene–DTAB–H₂O to those reported for the microemulsions based upon CS₂ added to 30 wt % DTAB solutions.³ The viscosity initially increases to a peak (at ϕ = 0.26) before decreasing, followed by a further, slower, increase as the phase boundary is approached. The conductivity decreases continuously with increasing ϕ but exhibits a plateau at compositions corresponding to the peak in the viscosity. It should be stressed that the 8 wt % microemulsion studied here does not lie in the region of the graph where rapid changes in viscosity take place.

(i) Dynamics of Styrene–DTAB–H₂O Microemulsions. Dynamics measured with the OHD-OKE technique from samples of neat styrene, styrene diluted 25 wt % in dodecane, and 8 wt % styrene encapsulated in a microemulsion are presented over two differing time scales in Figure 1. Dodecane was chosen as the solvent for the dilution studies because it represents the closest available analogue of the hydrophobic dodecyl chains of DTAB.

Figure 1a shows the OKE responses of the three samples over the first 1.5 ps. As with the previous work on CS₂,³ it is

TABLE 1: Results of Fitting OHD-OKE Data to Equation 1 (Except Oligomer and Polystyrene which Were Fitted to a Single-Exponential Decay)^a

sample	$a_1/(a_1 + a_2)$ (%)	τ_1 (ps)	τ_2 (ps)	η^b ($\times 10^{-3}$ kgm $^{-1}$ s $^{-1}$)	V (\AA^3)
styrene	50	1.26	9.5	0.695 ^c	56
25 wt % styrene in dodecane ^d	78	3.11	32.3	0.908	146
25 wt % styrene in CCl $_4$ ^e	58	1.76	9.7	0.864	46
8/20 styrene microemulsion	49	2.45	9.2	5.710	
toluene	55	1.17	5.3	0.560 ^c	39
25 wt % toluene in dodecane	80	1.90	19.4	0.845	95
25 wt % toluene in CCl $_4$	76	0.75	4.9	0.816	25
25 wt % bibenzyl in dodecane	79	1.69	23.0	1.265	75
25 wt % bibenzyl in CCl $_4$	79	1.90	23.6	1.516	64
15 wt % oligomer ^f in CCl $_4$	100	1.07			
10 wt % PS ^g in CCl $_4$	100	0.93			

^a Also shown are viscosity data and hydrodynamic volumes calculated using eq 2. ^b At 298 K. ^c Reference 82. ^d Viscosity = 1.383×10^{-3} kgm $^{-1}$ s $^{-1}$ at 298 K (ref 82). ^e Viscosity = 0.908×10^{-3} kgm $^{-1}$ s $^{-1}$ at 298 K (ref 82). ^f (–CPhH–CH $_2$ –) $_8$. ^g (–CPhH–CH $_2$ –) $_n$.

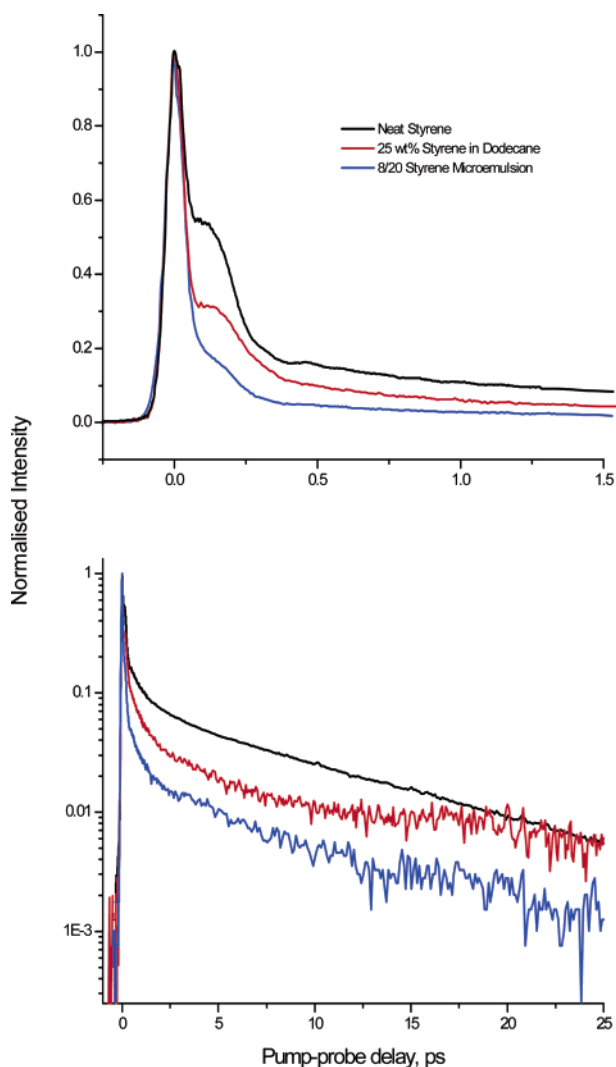


Figure 1. OHD-OKE traces of neat styrene, styrene diluted in dodecane and 8 wt % styrene dispersed in a DTAB microemulsion. Data are shown on ultrafast (top) and picosecond time scales (semilogarithmic scale).

noticeable that both the dissolved styrene and the microemulsion-constrained styrene yield traces of the same general form as neat styrene. In each case, there exists an intense signal around zero time delay, which is attributable to the electronic response of the liquids and contains no nuclear dynamical information, but instead reflects the instrument response function. Between pump–probe delays of 100–300 fs, each sample displays a substantial shoulder, the intensity of which varies

proportionally to the concentration of styrene. This provides an indication that the measured OHD-OKE signals are dominated by the response of the dispersed styrene. We have shown elsewhere that the OHD-OKE signal due to a DTAB–H $_2$ O solution is negligible.³ Also noticeable in Figure 1a is a slight shift to longer time delay for the peak of the shoulder of the dodecane-solvated sample, relative to the neat and microemulsion data. This shift is however somewhat difficult to discern, and such differences are more easily observed on transformation to the frequency domain. The deconvoluted and transformed data are described below, after consideration of the picosecond dynamics of these samples (Figure 1b).

Beyond 1.5 ps (Figure 1b), each trace can be well represented by the following function:

$$r_{\text{diff}}(t) = [a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)][1 - \exp(-2\omega_{\text{av}}t)] \quad (1)$$

where ω_{av} is the mean frequency of the spectral density.^{20,22} This function has been found to accurately describe the picosecond dynamics of several liquids and solutions.^{4–6} The slower of the two relaxation times can often be ascribed to orientational diffusion. The shorter relaxation time is generally too fast to be attributed to molecular reorientation but does appear to scale with the slower relaxation time. This relaxation has been assigned to motional narrowing by Fourkas et al.⁴⁹ The results of fitting the data in Figure 1b to eq 1 are presented in Table 1. Styrene exhibits dynamics that are well represented by the biexponential relaxation (eq 1) with a slower (orientational) relaxation time of 9.5 ps. Upon dissolution in dodecane, both relaxation times become slower, and the weight of the faster component becomes larger.

The assignment of the longer relaxation times to rotational diffusion is supported by the fact that, in simple liquid mixtures, they scale with the measured viscosities.⁶ It is therefore instructive to consider the measured relaxation times in terms of the Debye–Stokes–Einstein (DSE) equation:

$$\tau_c = \frac{g_2 V \eta}{kT} \quad (2)$$

in which τ_c is the collective reorientation time, measured by OHD-OKE (and other Raman techniques), g_2 is the static orientational pair correlation parameter, which scales between the collective and single molecule relaxation times (as measured by NMR for example), and V is the hydrodynamic volume.^{50,51} Assuming g_2 to have a value of unity and taking τ_2 (Table 1) equal to τ_c , this equation predicts a hydrodynamic volume of 56 \AA^3 for neat styrene and 46 \AA^3 for styrene dissolved in CCl $_4$

(the CCl_4 data will be discussed in more detail below). In contrast, the data for the 25 wt % styrene–dodecane mixture yields a value of 146 \AA^3 . This indicates a large discrepancy between eq 2 and the observed dynamics, which cannot be explained by a change in the g_2 parameter; in order that the data satisfy eq 2, g_2 would have to increase upon dilution, an unexpected result. The implication of this is that styrene–dodecane has, with respect to the DSE equation, an anomalously long τ_2 .

In recent studies of CS_2 dissolved in alkane solvents of chain lengths longer than seven carbon atoms,^{3,27} it was suggested that the rotational dynamics become nonexponential as a result of coiling of the solvent chains, leading to the creation of a heterogeneous environment in the mixture. Although the size of styrene in comparison to CS_2 might appear to preclude the formation of pools of bulk-like styrene, it is nonetheless apparent from the data in Figure 1b that the dynamics of dodecane-solvated styrene are markedly more dispersive than those of bulk styrene. Thus, the formation of a heterogeneous solution in this sample cannot be ruled out.

A second possible origin for these nonexponential relaxation dynamics is a contribution from the solvent. Although dodecane exhibits a nonzero OHD-OKE response, with dynamics on the picosecond time scale, we found that the signals from the samples discussed here are dominated by the response of styrene, even at delay times of 25 ps, the solvent signals being much weaker. Thus, with our current signal-to-noise, subtraction of the weak solvent response from the long time data⁵² was deemed unnecessary.

It is interesting to compare the value of the hydrodynamic volume obtained from eq 2 for neat styrene with the volume of 104 \AA^3 calculated from the van der Waals surface.⁵³ The discrepancy is probably due to the dependence of the hydrodynamic volume on both the axial ratio and choice of stick or slip boundary conditions, either of which can easily give rise to a factor of 2 change in V .⁵⁴ The above hydrodynamic volume was calculated using stick boundary conditions, because the slip boundary condition requires a choice of the axial ratio to be made. A simple comparison of hydrodynamic volumes calculated applying the stick boundary conditions is sufficient for this paper.

In contrast to the styrene–dodecane sample, the long time scale dynamics of microemulsion-constrained styrene are rather similar to those of bulk styrene, producing a biexponential decay profile with a very similar rotational diffusion time to that of the neat liquid (Table 1). In addition, a slowing of the shorter time constant is apparent. Thus, τ_1 in the microemulsion does not appear to scale with the orientational relaxation time, as might be expected from numerous simpler liquid systems.⁶ This suggests a more complex orientational relaxation in the microemulsion, compared to neat styrene.

As was also observed in the case of the CS_2 –DTAB– H_2O system,³ the picosecond dynamics of styrene in the microemulsion do not scale with the macroscopic viscosity of the sample. This is particularly obvious given the much higher viscosity exhibited by the microemulsion sample, compared with neat styrene. The reason for this is that the macroscopic viscosity of the sample is determined by intermicelle interactions. These are evidently decoupled from the dynamics of the confined styrene.

To discuss the dynamics of these samples more fully, it is desirable to transform the data into the frequency domain. A general Fourier transform–deconvolution technique for OHD-OKE data was developed by McMorro and Lotshaw and their co-workers^{4,20,23} and has been used by many groups.^{37,42,54–68}

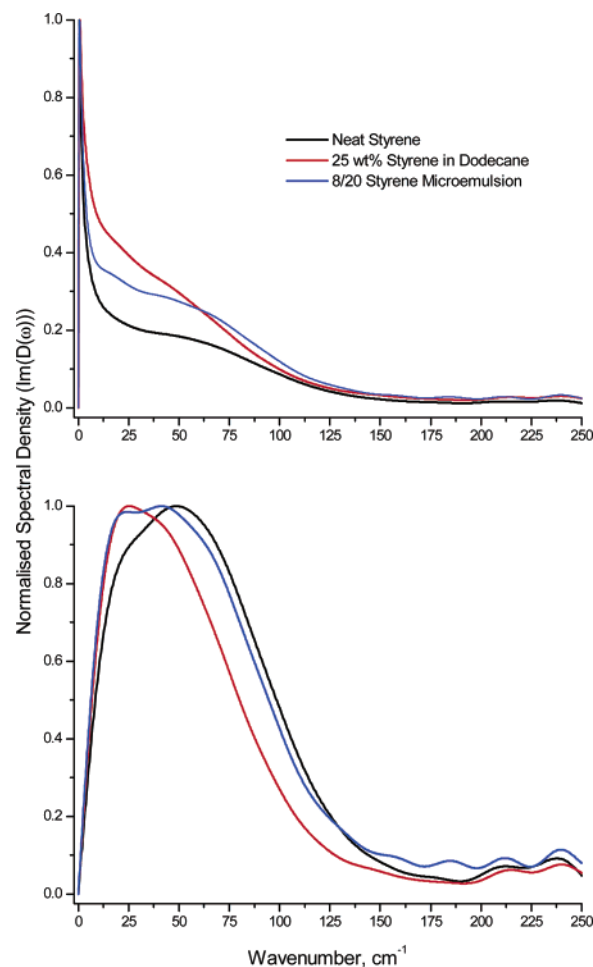


Figure 2. Complete (top) spectral densities of neat styrene, styrene diluted in dodecane and styrene dispersed in a microemulsion. Reduced (bottom) spectral densities of neat styrene, styrene diluted in dodecane, and styrene dispersed in a microemulsion.

A detailed description of the approach employed here can be found in previous publications,^{3,6} but, briefly, the spectral density, undistorted by the finite instrument response time, is obtained from the imaginary part of the ratio of the Fourier transform of the OHD-OKE data to that of the second-order autocorrelation of the laser pulse. To focus on the ultrafast dynamics, the reduced spectral density is generated by first subtracting from the data that portion fit by eq 1. In that case, the procedure yields just the portion of the Raman spectral density attributable to nondiffusive motion, for example librational and intermolecular (interaction-induced) relaxation.⁶ The justification for this procedure is the assumed time scale separation between ultrafast and diffusive dynamics. Because this assumption is somewhat questionable, at least in the case of the shorter exponential relaxation times, we present here both complete and reduced spectral densities.

The complete and reduced spectral densities for the three samples featured in Figure 1 are shown in Figure 2, parts a and b, respectively. All three of the complete spectra exhibit a sharp peak at very low frequency, arising from the slow rotational dynamics, and a broad shoulder at higher frequency. The higher frequency shoulder may arise from both molecular reorientational (librational) motion and intermolecular (collision and interaction-induced) relaxation. However, in the case of many liquids, including benzenoid aromatic liquids, there is evidence that the major component arises from librational motion.⁵⁴

The neat styrene and microemulsion samples have a higher librational frequency than the styrene–dodecane sample. This feature is more obvious in the reduced spectral density (Figure 2b). In comparison to the neat styrene, the spectral density of dodecane-solvated styrene has narrowed and shifted to lower frequency. This behavior has been observed previously in solution studies of polarizable OKE active solutes in non-polarizable solvents.^{3,27,54,69,70} In line with these earlier conclusions, we attribute this shift to the replacement of styrene nearest neighbors in the bulk liquid with less polarizable alkane molecules. This in turn leads to a shallower librational potential well and hence a lower librational frequency. This harmonic oscillator approach, discussed in detail by McMorro and Lotshaw²⁹ and Duppen and co-workers,^{69,71} has been successfully applied to the CS₂–DTAB–H₂O microemulsion³ and other solutions.^{29,52,69}

The reduced spectral density of the styrene microemulsion exhibits two maxima, in contrast to the single peak of the bulk and solvated samples. The lower frequency of the dispersed styrene peaks lies at around 10 cm⁻¹ close to the peak in the spectral density of the solvated sample. The higher frequency peak, at around 40 cm⁻¹, corresponds more closely to the bulk liquid profile. Also, the high frequency edge of the dispersed phase spectrum is close to that of neat styrene. Additionally, the microemulsion spectral density has a line width closer to that of the neat liquid than the narrower solvated sample. Thus, the reduced spectral density of the microemulsion contains features similar to both neat styrene and styrene diluted in nonpolar solvents, suggestive of an inhomogeneous site distribution.

It is instructive to compare these findings to those of our earlier study of CS₂–DTAB–H₂O microemulsions.³ There the CS₂ microemulsion environment was reported to be intermediate between bulk and solvated CS₂. It appears that, although by no means totally bulk-like in character, as indicated by the low frequency edge of the nondiffusive spectral density, microemulsion-constrained styrene possesses significantly more bulk-liquid character than CS₂ in the analogous microemulsion. The differences between styrene and CS₂ systems are also evident in the rotational relaxation times. For dispersed styrene, τ_2 is the same as that for bulk styrene, within experimental error. In contrast, microemulsion-constrained CS₂ exhibited orientational relaxation times more similar to those of dodecane-solvated CS₂. These clear differences lead to the conclusion that the dynamics of a given liquid dispersed within a microemulsion are determined by the dispersed species itself, as well as the properties of the micellar environment. We are currently investigating a range of liquids dispersed in DTAB with a view to further characterizing this observation.

Also evident in the reduced spectral densities are the intramolecular modes of styrene (which may also be discerned as underdamped oscillations in the data of Figure 1). These lie at 212 and 241 cm⁻¹ and are clearly visible in the neat and dilute samples. These bands are fully reproducible and are assigned to the ν_{41} and ν_{29} out-of-plane and in-plane bending modes of the vinyl group, respectively.^{72,73} The lower concentration of styrene in the microemulsion renders the intramolecular modes less obvious. The oscillatory features that are seen in the microemulsion spectral density in Figure 2b arise from Fourier transform artifacts which occur when signal-to-noise is low; these features are not reproducible.

(ii) Dynamics of Polymerized Styrene–DTAB–H₂O Microemulsions. The OHD-OKE data for a styrene–DTAB–H₂O microemulsion before and after polymerization are presented

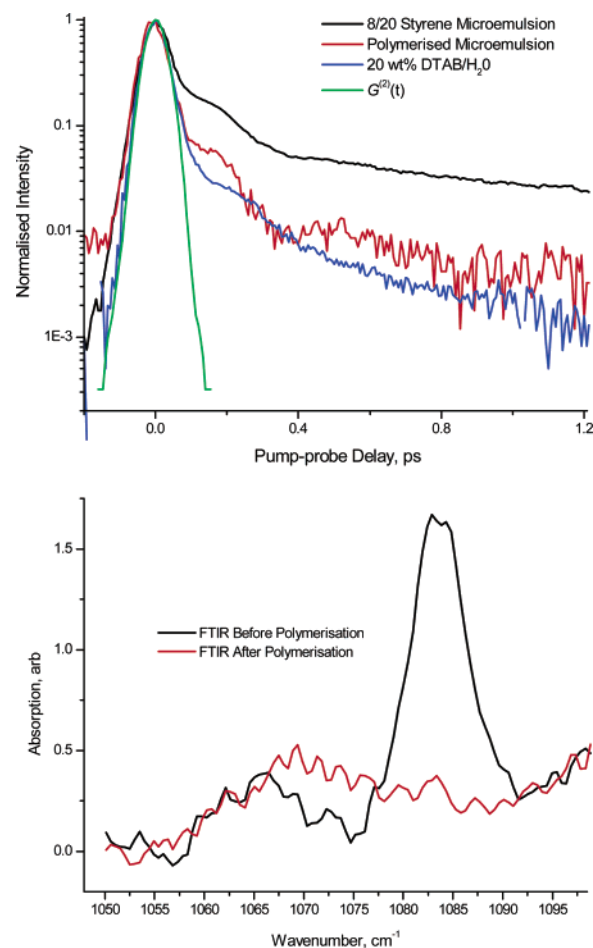


Figure 3. Semilogarithmic plots of OHD-OKE traces of styrene dispersed in a microemulsion, polystyrene-containing microemulsion, 20 wt % DTAB–water mixture, and pulse autocorrelation (top). FTIR spectra near 1085 cm⁻¹ of styrene-containing microemulsion before and after polymerization reaction (bottom).

in Figure 3a. Figure 3b shows FTIR spectra of the same microemulsion samples. The extent of polymerization was monitored by the decrease in absorbance of the monomer peaks, the product peaks being harder to observe. The peak due to styrene at 1083 cm⁻¹ clearly disappears as a result of the reaction, suggesting almost complete conversion to the polymer.

Also depicted in Figure 3a, for comparison, are the pulse autocorrelation function and OHD-OKE traces from a solution of 20 wt % DTAB, effectively a background trace for the microemulsion samples. The 8 wt % microemulsion OHD-OKE trace is also shown. At short pump–probe delay times, the polymerized sample exhibits a weak shoulder (relative to the monomer), followed at slightly longer delay times by a fast exponential decay with a time constant on the order of 200 fs. The latter is similar to that observed for the empty DTAB micelles, though at delays less than 200 fs the two traces are distinct.

The magnitude of the nuclear part of the OKE signal has clearly been dramatically reduced as compared to that of the unpolymerized system. This is initially a surprising result, given that there has been no change in the number of benzene units in the sample and that it is these units that are expected to dominate the polarizability of the polystyrene molecule. Thus, the data of Figure 3a suggest that the polarizability anisotropy relaxation in the polymer is accelerated compared to that of the microemulsion dispersed monomer.

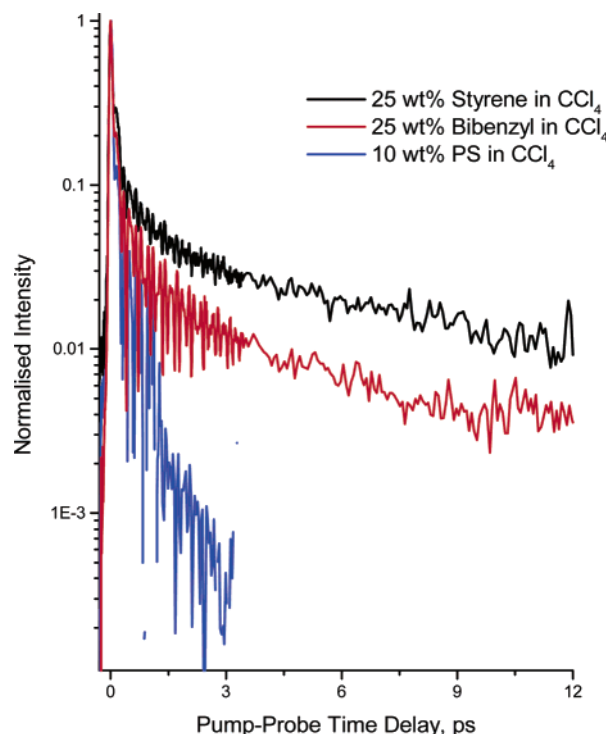


Figure 4. OHD-OKE data for 25 wt % styrene, bibenzyl and 10 wt % polystyrene dissolved in CCl_4 in semilogarithmic format, showing the quenching of the picosecond response as molecular weight increases. The high-frequency oscillations are due to the intramolecular modes of the solvent.

As mentioned in the Introduction, previous studies of the ultrafast responses of polymers are relatively few in number. Most relevant here is the work of Sengupta et al.⁴³ on poly(2-vinylnaphthalene). They reported that the transient grating optical Kerr effect (TG-OKE) signal from this polymer showed a very fast decay of around 140 fs in the solid phase and 190 fs in CCl_4 solution. In addition, the dilute sample exhibited a biexponential decay, with time constants of 1 and 9 ps, which were absent in the solid. Because the relaxation times observed did not obey the predictions of eq 2, it was concluded that the observed relaxation was due to librational motion of the naphthyl side groups, rather than rotational diffusion of the polymer molecule as a whole. The data for the latex particles, where a slow component is absent (Figure 3a) are consistent with this model. A more detailed study of some analogous systems is made in the next section.

(iii) Dynamics of Structural Analogues of Polystyrene in Solution. The purpose of this series of experiments was to address the two main issues raised by the dynamics of the polymerized microemulsion (Figure 3): the considerable decrease in signal intensity between 100 and 300 fs, and the apparent lack of any dynamics on a picosecond time scale. By studying the dynamics of toluene, styrene, bibenzyl, an oligomer of polystyrene with 8 constitutional repeat units and polystyrene itself, the effects of an increased chain length on the dynamics should become apparent. Each solute was studied, where possible, in two solvents, dodecane and carbon tetrachloride, at dilutions of 25 wt %. Exceptions were the oligomer and polystyrene itself which proved insoluble in dodecane and soluble only to 15 and 10 wt % in CCl_4 respectively.

The picosecond time domain results are presented in Figure 4 and Table 1. In the case of styrene, toluene and bibenzyl the data between 1.5 and 30 ps were fitted to eq 1. In contrast the

dynamics of the oligomer and polystyrene samples were markedly different, with the longer component being essentially suppressed.

For styrene, toluene, and bibenzyl, the picosecond time scale dynamics reveal a major 1–3 ps relaxation, with a further relaxation on the scale of five to tens of picoseconds. The observed relaxation times of neat toluene are in good agreement with the previous study of Chang and Castner.³⁷ As was observed for the polymerized polystyrene in the microemulsion (Figure 3a), the picosecond rotational dynamics are essentially absent for the oligomer and polystyrene; only a very fast, ca. 1 ps, relaxation is observed in this time window.

Using the τ_2 and η data for the styrene in CCl_4 solution in eq 2 yields a value of 46 \AA^3 for the hydrodynamic volume, which is only slightly lower than the value for neat styrene (see above and Table 1). The anomalous behavior of the dodecane-styrene mixture has been referred to above. In the case of toluene, a similar pattern is observed: the data yield hydrodynamic volumes for toluene of 39, 95, and 25 \AA^3 for the neat, dodecane, and carbon tetrachloride samples, respectively. Once again, the neat and CCl_4 values are similar, but the dodecane sample gives a significantly higher volume. We conclude that these data are further evidence that long chain alkyl solvents yield anomalously slow orientational relaxation times. The origin of this behavior is, as yet, unclear, although we, and others, have speculated that the dodecane solution may be inhomogeneous at a microscopic level.

In the case of bibenzyl, the orientational dynamics observed in the two solvents are rather similar, with τ_2 being almost the same within experimental error. The resulting hydrodynamic volume of 75 and 64 \AA^3 for dodecane and CCl_4 solvents, respectively, are consistent with those obtained for toluene and styrene in carbon tetrachloride, i.e., $V_{\text{bibenzyl}} \approx 2V_{\text{toluene}}$. It is interesting to note that the discrepancy between the hydrodynamic volume of bibenzyl in dodecane and that in CCl_4 is much smaller than was observed for styrene and toluene. A possible explanation for this is that the large size and flexibility of the bibenzyl molecule prevents, or at least reduces, the inhomogeneity to which the non-hydrodynamic behavior of other solutes in long alkane chain solvents was attributed.^{3,27}

The values of τ_1 given in Table 1 are too fast to be associated with molecular reorientation.⁵⁴ They do however show an identical trend to τ_2 , namely, an increase in τ_2 is always accompanied by an increase in τ_1 . This is consistent with previous studies of binary solutions which have noted a correlation between fast and slow components of the biexponential relaxation profiles.⁴⁹

Figure 5 shows the complete spectral densities for each of these samples dissolved in CCl_4 . By preparing the samples using weight percentages rather than molar dilution, samples were obtained with similar numbers of phenyl side groups, making a comparisons of relative peak heights approximately valid. In each case, the spectral density has been normalized to the intensity of the intramolecular CCl_4 band located at 220 cm^{-1} in order to gauge the relative intensities of the low-frequency responses of each of the samples. Though the lower dissolved concentrations of the oligomer and polystyrene must be taken into account, there is evidence in Figure 5 for a decrease in the intensity of the spectral density as molecular size and complexity increases. Conversion of the wt % data in Figure 5 to mole fraction of phenyl groups present is perhaps more rigorous, though the multiple contributions to the spectral density make normalization somewhat arbitrary. Conversion following nor-

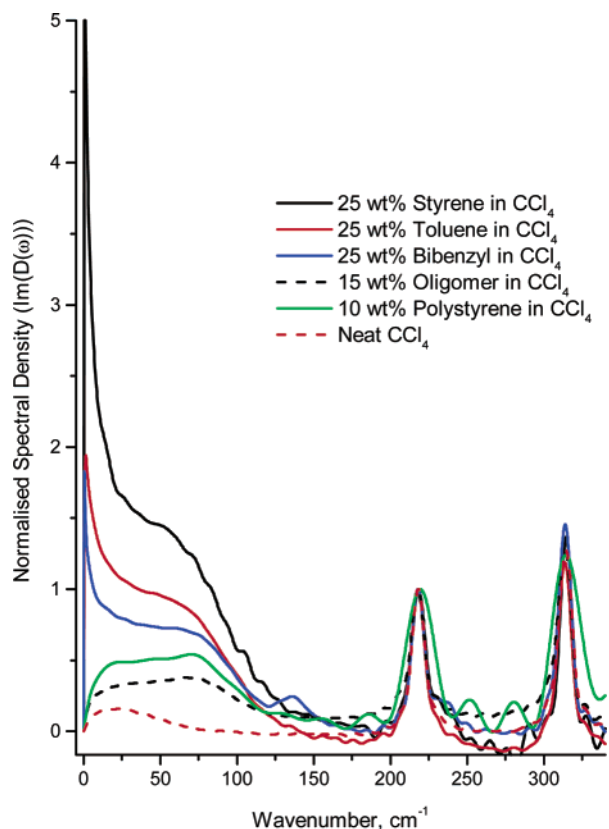


Figure 5. Complete spectral densities of structural analogues of polystyrene dissolved in CCl_4 normalized to CCl_4 peak at 220 cm^{-1} .

malization at 50 cm^{-1} (the librational region) also led to a decrease in intensity in the order $I_{\text{bibenzyl}} > I_{\text{oligomer}} > I_{\text{polymer}}$.

The lack of any picosecond time scale dynamics in the oligomer and polymer samples is apparent, from comparison with the sharp, low frequency peaks exhibited by styrene, toluene, and bibenzyl. The loss of this low frequency band is accompanied by a shift in the spectral density to higher wavenumbers. This is particularly evident in the oligomer and polymer samples but is also observed in the bibenzyl spectral density. In each case, the observation of increasing frequency with increasing molecular size means that these bands are highly unlikely to be associated with molecular librations. Rather, we suggest that they are of intramolecular origin. Low-frequency Raman studies of solid polystyrene,^{74,75} using frequency-domain techniques, report vibrational bands between 50 and 70 cm^{-1} , in addition to low-frequency boson peaks between 10 and 20 cm^{-1} . In each case, the vibrational band has been assigned to a torsional mode of the phenyl rings about the carbon chain backbone.^{74,75} We therefore assign the high-frequency portion of the oligomer and polymer spectral densities in Figure 4 to the activation of these intramolecular modes. Furthermore, the small peak present in the bibenzyl spectrum at $70\text{--}75\text{ cm}^{-1}$ can also be attributed to a similar vibrational mode. It is interesting to note the presence of an additional intramolecular mode in the bibenzyl spectral density at 135 cm^{-1} although the assignment of this mode is unclear.

IV. Discussion

As discussed above, the microemulsion spectrum bears a close resemblance to that of neat styrene. Thus, and in analogy with the assignment for other monosubstituted benzene liquids, the broad line shape around 50 cm^{-1} may be ascribed to a molecular libration in a cage of nearest neighbors. The weak ultrafast OKE

response of polystyrene formed in the polymerized microemulsion (Figure 3) has prevented the generation of the corresponding spectral density. However, the absence of any significant intensity around 300 fs , which is assigned to an overdamped librational mode in liquid styrene, and of any picosecond time scale relaxation, suggests that this sample has more in common with the oligomer and polymer solutions than with toluene, styrene, or bibenzyl.

Considering the data presented here as a whole, it is clear that, as the molecular size and complexity increases, a suppression of molecular librational modes has occurred, in favor of the excitation of low frequency intramolecular torsional modes of the carbon chain backbone. This is reflected in a shift to higher frequencies of the Raman spectral densities for bibenzyl, the oligomer, and the polymer. This is not a surprising observation, given that, as molecular size and flexibility increases, it becomes increasingly difficult to define what is represented by librational motion. The work of Sengupta et al. on poly-(2-vinylnaphthalene)⁴³ reported relaxation via librational motion of the naphthyl side groups (i.e., an intramolecular libration). The data presented here are consistent with the assignment of Sengupta and co-workers.⁴³ However, the higher time resolution used here enabled recovery of the Raman spectral densities. From these we have assigned the intramolecular motions as high-frequency torsional modes of the molecule, which incorporate twisting of the carbon-chain backbone in concert with the side group "libration".

We have also investigated the solvent polarizability dependence of the spectral densities of toluene, styrene, and bibenzyl, in an effort to shed further light on their origin. Figure 6 shows the reduced spectral densities of these three molecules in dodecane and in CCl_4 solution, along with that of the neat liquid, where appropriate. The lack of solubility of the oligomer and polymer prevented their inclusion in the comparison. In the cases of both toluene (Figure 6a) and styrene (Figure 6b), a clear difference exists between the librational line shape resulting from the dodecane solution and that from the CCl_4 sample. The former is narrower and shifted to lower frequency as compared to the neat liquid, whereas the latter exhibits very little variation from the bulk liquid. Clear differences also exist in the bibenzyl spectra between dodecane and CCl_4 solvents (Figure 6c); again that of the dodecane solvated sample is narrower and shifted to lower frequency.

The reason for the shift in the spectral density in dodecane has been discussed above and elsewhere and can be attributed to a reduction in the librational frequency on dilution. Such behavior is well described by the harmonic oscillator model introduced by McMorro and Lotshaw²⁹ and Duppen et al.^{69,71} That no similar change takes place when the solvent is the more polarizable CCl_4 is evidence that the shift of librational frequency on dilution is related to the strength of the solvent-solute interaction. The harmonic oscillator model leads one to expect a shift to either higher or lower frequency depending on whether the solvent-solute interaction is stronger or weaker respectively than the solute-solute interaction.²⁹ In the event of the solvent being less polarizable than the solute, the solute-solute interaction is the greater, leading to a shift to lower frequency of the librational band with increased dilution. This is the case for almost all OHD-OKE experiments using alkane solvents and was also observed in the study of CS_2 dissolved in CCl_4 by Samios and Mittag.⁷⁶ Conversely, in the event of a highly polarizable solvent being used, the librational frequency would be expected to be shifted to higher frequency. Thus, the unshifted spectra for polarizable aromatic solutes, such as

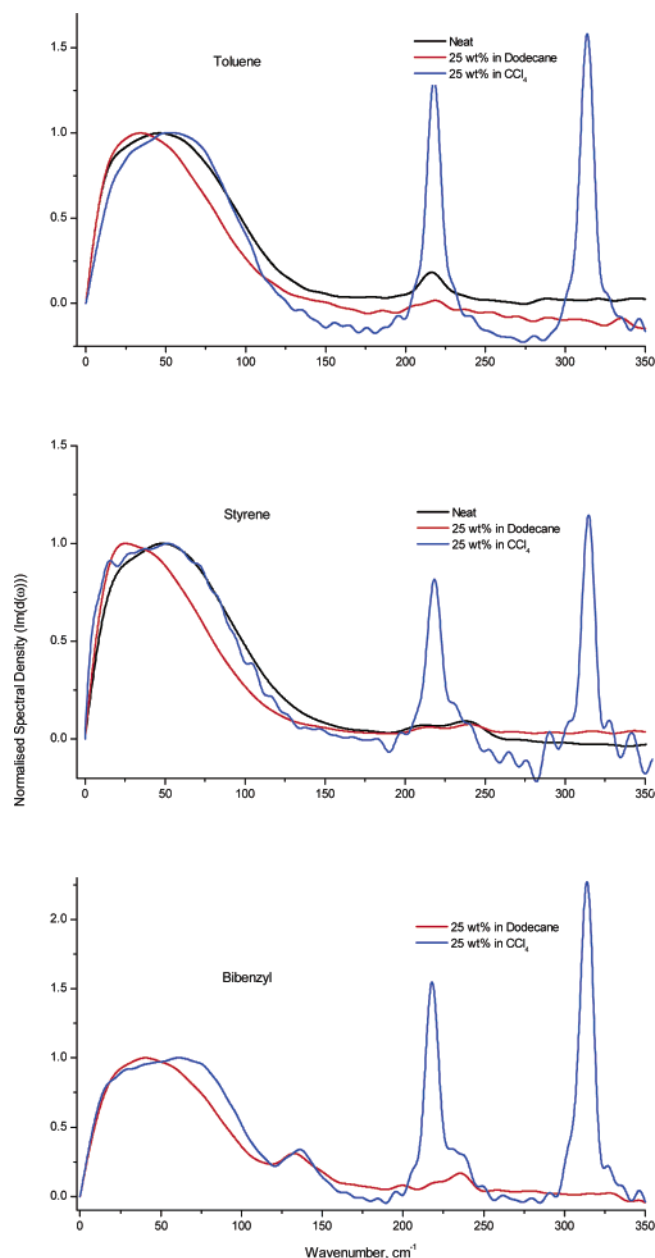


Figure 6. Reduced spectral densities of (top) toluene, neat and dissolved in CCl_4 and dodecane; (center) styrene, neat and dissolved in CCl_4 and dodecane; and (bottom) bibenzyl dissolved in CCl_4 and dodecane.

styrene, in the polarizable CCl_4 solvent, are fully consistent with the harmonic oscillator model. A similar result, an unshifted spectral density of benzene in CCl_4 , was reported by McMorro and Lotshaw.⁷⁷

It should, however, be noted that, although these results are fully consistent with an assignment to molecular librational motion, this may not represent a definitive explanation. The possibility exists that the shift to lower frequency upon dilution may also be caused by the removal of interaction-induced (II, dipole-induced-dipole, and collisional) effects, which are often assumed to contribute to the spectral density at higher frequency. These too would be expected to persist in the event of a polarizable solvent such as CCl_4 being used for dilution. Thus, it is not possible to distinguish between these effects with the present data. Recent progress in the separate determination of orientational and II contributions to the line shape suggest the possibility of a more definite assignment in the future.⁷⁸

The fact that both bands in the spectral density of bibenzyl at 75 and 135 cm^{-1} also shift to lower frequency upon dilution in dodecane indicates that intra- as well as intermolecular modes are susceptible to solvent-solute interactions. Such shifts of intramolecular modes are often observed in matrix isolation studies and, indeed, on moving from gas to liquid phases.^{79,80} However, relatively little is known about variations in low-frequency modes due to changes in solvent properties. This is the subject of a separate publication.⁸¹

V. Conclusions

A study of the ultrafast dynamics of styrene dispersed as the oil phase in a DTAB-water microemulsion before and after polymerization has been carried out. It has been observed that dispersed styrene exhibits inhomogeneous dynamics, with a significant component similar to those of the bulk liquid. This was rather different to the behavior reported for microemulsion-dispersed CS_2 .³ Thus, it appears that the dynamics of the dispersed component depend on the extent of its interaction with the micelle.

Following polymerization to form dispersed nanolatex particles, the amplitude of the OHD-OKE signal was found to decrease significantly and to exhibit a much faster relaxation. Subsequent studies of several structural analogues of polystyrene in solution showed that this could be attributed to the increased size of the polymer, resulting in a number of additional relaxation pathways via intramolecular modes becoming accessible. The torsional mode of the polymer about the carbon chain backbone was found to be particularly important. These findings on the dispersed polymer are consistent with earlier work carried out on poly(2-vinylnaphthalene) in solution by Sengupta et al.⁴³

The picosecond time scale dynamics have been discussed in terms of the DSE model. In the microemulsion dispersed styrene, the orientational relaxation time was not very different to that of bulk styrene. However, in solution studies, further evidence was found for the non-hydrodynamic behavior of solute reorientation in long-chain alkane solvents, as reported previously.^{3,27} This effect, observed for styrene and toluene dissolved in dodecane, was diminished in the case of bibenzyl, indicating a possible relation to the size of the solute molecule.

Finally, a solvent-related variation in the low-frequency Raman spectral density has been observed for styrene, toluene, and bibenzyl. This has been attributed to the relative polarizabilities of the solvent and solute molecules, in accordance with the harmonic oscillator model.^{29,69,71} Though these observations were made mainly on librational bands, small shifts have also been observed in low-frequency modes assigned to intramolecular motion.

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