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## Abstract

We report measurements of the glass transition temperature ($T_g$) in thin free-standing polymer films of polystyrene (PS) by means of confocal Raman spectroscopy. The paper introduces Raman spectroscopy as a novel method for the determination of $T_g$ in polymer thin films. We find excellent agreement between Raman scattering and previously reported values of $T_g$ obtained from either Brillouin scattering or ellipsometry. Further possible applications of the method to more complex conjugated polymers are briefly discussed.

## 1. Introduction and overview

Objects with certain geometrical properties interacting with each other and displaying cooperative effects or phase transitions constitute a very general problem in physics, including systems as varied as colloidal fluids, hard-rod models for lyotropic and thermotropic liquid crystals (LCs), and polymers. An important characteristic (besides the influence of external fields and/or boundaries) is the presence of a *natural length scale* ($L$) related to the size of the interacting objects: when the system is confined by boundaries within a region comparable to or smaller than $L$, cooperative phenomena can be greatly affected.

Polymers are well suited to study these phenomena: they come in a wide variety of structures; have several different phases (glassy, LC, crystalline and isotropic); and can be easily manufactured in structures with dimensions comparable to the size of individual polymer chains. In addition, they can be monitored with a wide variety of non-invasive optical techniques.

The glass transition (GT) in polymer thin films has been the subject of intense interest in the last few years, not only as a problem of fundamental physics within the above mentioned framework, but also due to its technological ramifications in polymer device physics. Below the GT the polymer behaves as a hard disordered solid with a microscopic glassy structure, while above it the polymer becomes rubber-like and comparatively softer, thus changing its

physical properties over time and beginning the outset of the crystallization process in many cases (if a crystalline phase exists above the GT).

Keddie *et al* [1, 2] pointed out that the effective glass transition in thin film geometries of polystyrene (PS) strongly depends on the film thickness ($d$) and the interfacial interactions. They reported that the glass transition temperature, $T_g$, of a PS thin film ($\sim$300 Å) supported by a Si substrate was depressed by $\sim$20 °C [3]. In a free-standing film with the same $d$, however, $T_g$ was depressed by $\sim$70 °C, thus showing clearly the role of interfacial interactions. Substrate interactions were also observed in a poly(methyl-methacrylate) (PMMA) film [4]. It was suggested that the boundary of the film had a surface layer of finite thickness with an increased mobility, producing a lower $T_g$. This high mobility layer increases as the temperature ($T$) approaches the bulk $T_g$ upon heating.

The origin of the increased mobility of the polymer chains at the surface layer is still unclear [5, 6], even though some theoretical understanding is emerging [7, 8]. Mayes [9] provided the first theoretical arguments linking the reduced $T_g$ with the mobility of this layer. Chain ends are in higher concentration at the interfaces (for entropic reasons) and this should reduce the overall mass density close to the interfaces. This phenomenon was predicted in a simulation by Rouault *et al* [10] and Müller *et al* [11]: the increased mobility of the chain segments is a consequence of the density reduction and leads to a smaller $T_g$ for the film. More recently, a different possible origin was proposed by de Gennes [5]. It was suggested that two dominant mechanisms exist in the dynamics: (i) standard chain (reptation) motions and (ii) collective motions. These motions are in constant competition and it is expected that the former dominates in the bulk for reasons of end-group hindrance. However, as $d$ reaches the size of the coil, the collective motion is expected to become dominant. The idea of two competing motions in polymeric systems may explain the reduction of $T_g$ in thin polymer films, but this is an area where more theoretical work and extensive simulations are clearly required.

On the experimental side, Brillouin scattering (BS) has been used [12] to measure the $T_g$ of free-standing PS films; $T_g$ values from BS measurements of the bulk are the same as those from differential scanning calorimetry (DSC). In addition, transmission-mode-nulling ellipsometry has been shown to measure the molecular weight dependence of $T_g$ in PS films [13]; contrary to BS the limitation for ellipsometry is that the relative sensitivity of the technique worsens as $d$ decreases. Forrest *et al* [14] have given an extensive account of previous experimental and theoretical work concerning the effect of the interface and confinement on $T_g$ for thin polymer films. The reader is referred to this important previous study for further details.

This paper introduces the use of confocal Raman spectroscopy (RS) to monitor $T_g$ in free-standing films with varying $d$'s and we use PS as a model study in which the technique can be validated. As far as we are aware, RS has not been used for this purpose before; it provides a very powerful, *in situ*, non-invasive method with high spatial resolution. The measured $T_g$ values for PS thin films are lower than those of the bulk and in excellent agreement with previous experiments. PS serves, accordingly, as a standard sample with which to test the validity of the method. A few other laser-based techniques are, in fact, being developed now for the study of glass transitions in polymer thin films, like the laser interferometry method developed by Diakoumakos and Raptis [15]. Raman microscopy has additional advantages though, for it provides simultaneously an *in situ* probe into inter- and intramolecular interactions through the self-energy of the monitored vibrations.

## 2. Experimental details

### 2.1. Experimental apparatus and samples

Spectra were collected with a Renishaw Raman spectrometer attached to a confocal microscope with a ×50, long working distance objective. Samples were placed inside a Linkham hot stage

with a temperature stability of $\pm 0.1\,°C$. Heating rates were $5\,°C\,min^{-1}$ and were the same for all samples. Polarized Raman intensities $I_{\parallel,\perp}$ were recorded after a dwell time of 100 s for each $1\,°C$ step to ensure equilibrium. Either a HeNe (633 nm) or a near-infrared diode (830 nm) laser was used. With the combination of a low-power ($<1$ mW), non-resonant laser excitation and measurements performed under a $N_2$ atmosphere, we can discount any effects from photochemical reactions (oxidation, cross-linking, etc). These effects are of minor significance here. The confocal distance of the microscope is larger than the average thickness, $d$, for our samples ($d \sim 0.05$–$0.10\,\mu m$). Integration times of 600 s were used. Raw spectra were fitted (Grams 32, Galactic Industries) to obtain shifts, FWHM data and integrated intensities of the peaks [16].

Thin free-standing PS films were prepared by spin coating at different speeds for different thicknesses onto KBr substrates. The substrates were dissolved in distilled water and the free-standing polymer films were then picked up with a $20 \times 20\,\mu m^2$ grid size copper mesh of the type used in electron microscopy. The nominal thicknesses, $d$, were measured with a Dektak profilometer. The mass concentrations of the solutions were 6 mg ml$^{-1}$ in toluene. The molecular weight ($\bar{M}_w$) and $R_{EE}$ of PS are 600 000 and 59 nm, respectively.

## 2.2. The method

The underlying idea of the method is straightforward: almost every phase transition will affect intramolecular vibrations through their self-energies by taking into account the interaction of specific modes with the electronic structure. The electronic structure, in turn, is affected by intra- and intermolecular interactions, which depend on the phase (solid, liquid, liquid crystalline, glass, etc) and, accordingly, on the temperature. Raman shifts, FWHM data and relative intensities of individual modes as a function of $T$ provide an indirect probe for structural phase transitions. A closely related example is the monitoring of transitions in LCs [17] by RS, but examples abound and include other types of phase transitions, like magnetic [18] or superconducting [19]. The basic principle is the same: changes in the phonon self-energies produced by magnon–phonon or electron–phonon interactions, which therefore reveal (indirectly) a phase transition in the magnetic or electronic excitations. The GT is particularly suited in that respect, for it is accompanied in polymers by a discontinuity in the thermal expansivity at $T_g$ which directly affects intermolecular interactions. A distinct *kink* is produced then in the temperature dependence of the self-energies of intramolecular modes which can be used to monitor the GT. Exactly the same principle, but for a different reason, holds in Brillouin scattering experiments [14] where the discontinuity in the thermal expansivity produces a characteristic kink in the sound waves monitored by the technique. The change in this latter case is more direct though, for the thermal expansivity affects directly the mass density $\rho$ and longitudinal elastic constant and, accordingly, the speed of sound [14].

RS combines several advantages. Spatial resolution $\sim 1\,\mu m$ (both in the $x$–$y$ sample plane and along the $z$ axis normal to the plane) is a significant one. For the sake of completeness, we briefly follow here our recent studies in [20, 21], keeping details to a bare minimum. The off-resonance scattering efficiency $I_R$ for an active Raman mode is given by [22] $I_R = |\vec{e}_S \cdot \hat{R} \cdot \vec{e}_L|^2$, where $\hat{R}$ is the Raman tensor for a specific vibration and $\vec{e}_L$ and $\vec{e}_S$ are the incident (laser) and scattered polarization directions, respectively. The *depolarization ratio*, $\rho = I_\perp / I_\parallel$, where $I_\parallel$ and $I_\perp$, are the parallel and perpendicular polarized intensities (with respect to the polarization of the exciting laser light), respectively, provides some information on the symmetry of $\hat{R}$, even in isotropic liquids. A mode is either depolarized ($\rho \neq 0$) or polarized ($\rho = 0$) in the case of totally symmetric ($\Gamma_1$) modes. Molecular liquids, in addition, display several cases in which the averaging rules of isotropic liquids are broken down. This reveals the presence of

*molecular order* and it provides an invaluable tool to monitor the physics of interfaces (where molecular order may exist) in LCs and polymers in situations where no other experimental technique is available [23]. $I_\perp$ and $I_\parallel$ themselves have information on the symmetry of the modes, though not normalized (to the total scattering cross section) as in $\rho$. $I_\perp$ and $I_\parallel$ provide the simplest tool to detect structural phase transitions.

There are several shortcomings for the technique though. Among them, the problem of differentiating surface from bulk phase transitions (depending on the penetration depth of the light, confocality, resonances, etc), as well as the impossibility of deducing long-range structural motifs from RS alone. A huge variety of phase transitions in polymers have not yet been studied with x-rays or neutrons and the effect of the structural phases on the vibrations is indirect and difficult to characterize.

## 3. Results

We concentrate on the Raman spectra of PS around $\sim$1100 cm$^{-1}$ as shown in figure 1(a). The data in figure 1(a) have been obtained on a 180 nm-thick free-standing PS film at room temperature with the 830 nm laser-diode excitation. The spectrum is dominated in this region by two main peaks around $\sim$1000 and 1183 cm$^{-1}$. The main Raman active modes of PS in other spectral regions have been studied in the past for different types of characterizations. Kellar *et al* [24] and Vittoria *et al* [25] have performed extensive studies of different Raman active modes in PS and, in particular, intensity ratios among several peaks as a way of characterizing the degree of residual crystallinity in the sample. Figure 1(b) shows, in addition, two images of free-standing films with two different thicknesses standing on top of copper meshes. The laser spot ($\sim$5 $\mu$m in diameter) is focused with the microscope right in the centre of one of these squares for the temperature scans. Films are very homogeneous in thickness, as revealed by large areas with a lack of colour fringes under white light illumination in the backscattering geometry.

The intensity of many Raman active modes will be affected by the exact amount of glassy and (residual) crystalline material within the as-prepared sample. This is the basis of the set of empirical rules discussed by Kellar *et al* [24] to determine the degree of crystallinity in a given sample. We choose to follow the 1183 cm$^{-1}$ mode of PS which has been shown to be remarkably independent of such effects. Still, the intensity will be affected at the GT temperature because of the discontinuity in the thermal expansivity and other physical properties directly affecting intermolecular interactions.

Figure 2 shows the key results of the application of the technique to PS. We monitor the frequency, the FWHM and the intensity for both parallel and perpendicularly polarized Raman signals in a 180 nm-thick free-standing PS film as a function of $T$ for the $\sim$1183 cm$^{-1}$ Raman active mode. A general trait is that Raman frequencies will soften, and peak widths will broaden, when $T$ is increased (due to anharmonic interactions). Figure 2 shows this expected general behaviour but also shows a distinct structure which is the signature of the GT. These features come from changes in the self-energies of the vibrations affected by the phase transition (and its discontinuity in thermal expansivity) and they are in excellent agreement with the temperatures at which the GT is expected to occur for this thickness in PS. As in the case of BS [14], a microscopic model is not available at the moment to explain these structures (i.e. the details of the shape of the feature), but their ultimate origin is very clear. The fact that a phase transition affects the intensities, FWHM data and frequencies is a simple manifestation of the fact that the self-energies of the modes are linked to all three of these parameters. Any of these magnitudes, or simple manipulations of them, can be used to identify the glass transition. For PS there is no distinct advantage in using polarized scattering, i.e. $I_\parallel$ and $I_\perp$ display essentially
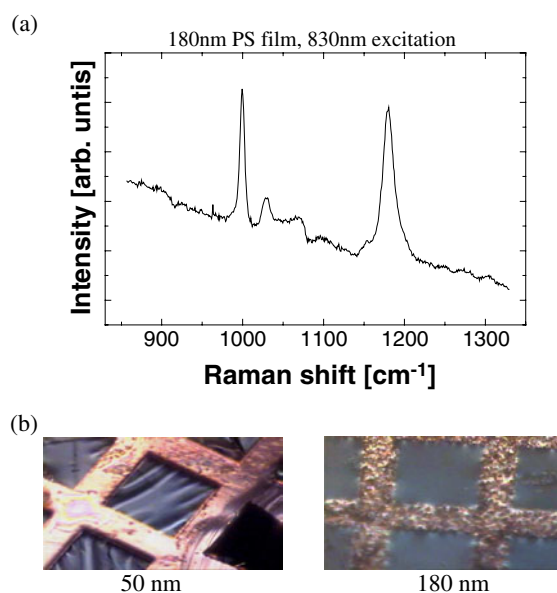
(a)



(b)



50 nm 180 nm

**Figure 1.** (a) Raman spectrum of a 180 nm-thick PS film obtained with a 830 nm diode laser between ∼900 and 1300 cm$^{-1}$. (b) Two free-standing films of PS with different thicknesses (50 and 180 nm) each placed on top of a copper mesh. Each square in the mesh is approximately $20 \times 20$ $\mu$m$^2$.

(This figure is in colour only in the electronic version)

the same qualitative information as can be appreciated from figure 2. This is because PS is a simple polymer and the experimental evidence shows that there is no surface molecular alignment in this case. But we will argue later that this not necessarily the case in general. We have evidence from more complex conjugated polymers in which $I_\parallel$ and $I_\perp$ display different transitions coming from either the surface or the bulk of the films. This adds an additional technical advantage to RS with respect to other experimental techniques. Figure 2 shows that the 1183 cm$^{-1}$ displays in both polarizations a relatively flat behaviour in the intensity with a distinct feature at the GT; this provides a very convenient tool to monitor the changes as a function of thickness. These features in the intensity are always followed by a corresponding softening of the frequency and broadening of the peak for increasing $T$'s for all thicknesses, as expected.

The equivalent experiment of figure 2 in a bulk PS sample obtained by rapid quenching from the melt shows a very distinctive feature at ∼105 °C, which is the nominal standard $T_g$ for bulk PS. For the films, however, the transition is always at lower temperatures and in excellent quantitative agreement with previous studies. To demonstrate this we follow closely in figure 3(a) the GT anomaly seen in $I_\parallel$ for different film thicknesses. We concentrate only on the results for $I_\parallel$, for the other data display essentially the same qualitative information, as seen in the example of figure 2. Figure 3(b) summarizes the results for the transitions. The GT is very easy to follow from the data and the result in figure 3(b) is in excellent agreement with BS and ellipsometric determinations of the GT for PS samples with similar molecular weights [14]. We consider the data in figures 2 and 3 as clear proof of principle for RS as a tool to monitor the GT in polymer thin films.
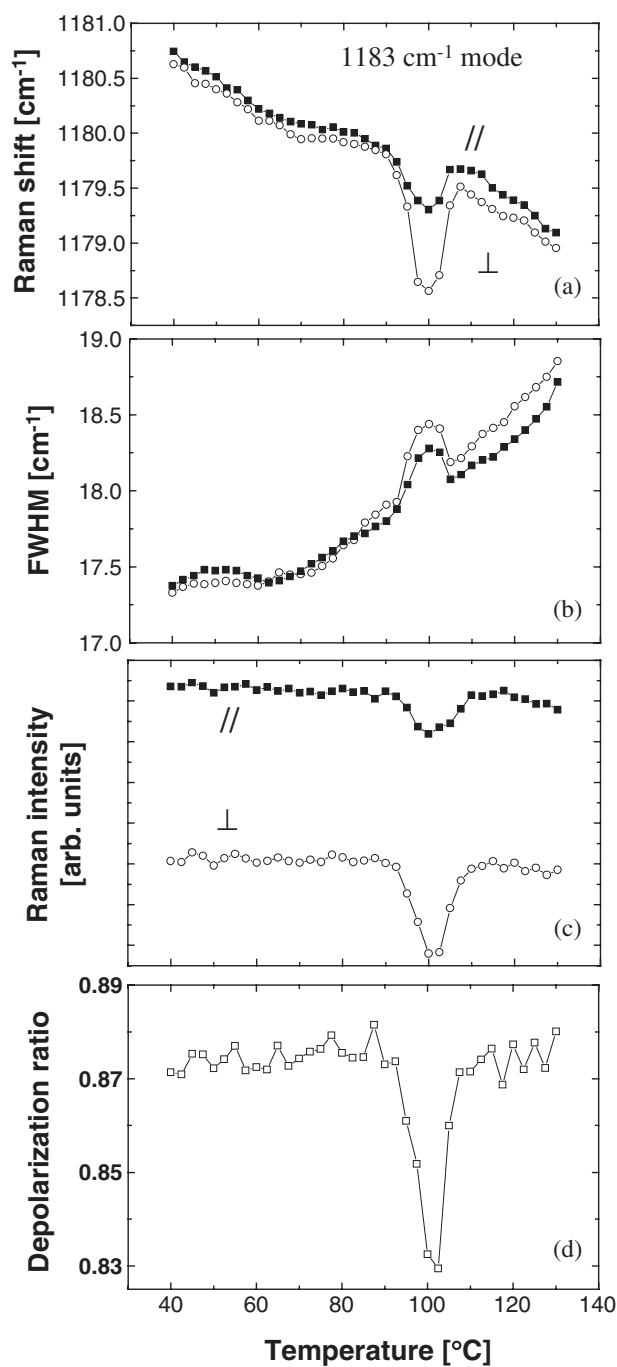
**Figure 2.** (a) Raman shift, (b) FWHM data, (c) polarized intensities and (d) depolarization ratio as a function of temperature for the 1183 cm$^{-1}$ mode of PS in the 180 nm film shown in figure 1(b). The data have been obtained with a HeNe laser. In (a) and (b) the frequencies and widths are shown for the two possible polarizations. The GT appears as a distinct feature in an otherwise monotonic softening of the frequency and broadening of the width produced by anharmonic interactions. See the text for further details.
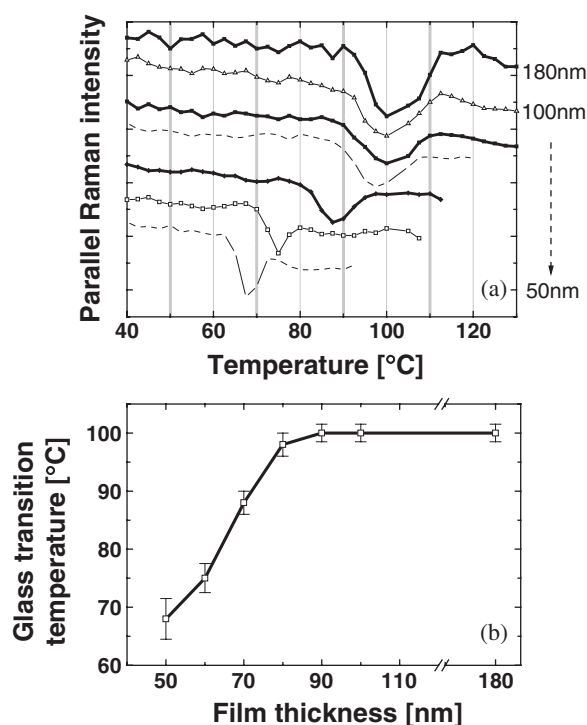
**Figure 3.** Parallel Raman intensity ($I_\parallel$) as a function of $T$ of PS for different film thicknesses going from 180 to 50 nm. In (a) the raw data can be seen while (b) summarizes the extracted GT temperatures. A distinct crossover is observed below a specific thickness, which depends on the molecular weight. The same type of behaviour is observed in BS for polymers with similar $\bar{M}_w$.

## 4. Conclusions

The main objective of this short paper is to establish the use of micro-Raman spectroscopy as an additional tool for studying the glass transition in thin polymer films. We have demonstrated its potential through a textbook example involving PS. Excellent agreement is found with previous determinations of $T_g$ by other techniques. We would like to finish this paper with a brief comment on further possibilities provided by the technique, which are not fully exploited in the case of PS due to its simple nature. As pointed out before, polarized scattering in PS gives essentially the same qualitative information for both $I_\parallel$ and $I_\perp$, but this is not necessarily the case in more complex polymers that may display molecular order at the surfaces. We have found evidence of this in thin films of the conjugated polymer poly(9,9-di((2-ethyl)hexyl)fluorene) (PF$_{2/6}$) [26–29].

We also found evidence of a crossover in which (i) two glass transitions are observed if $R_{EE} < d$ ($d$ = thickness of the film) or (ii) only a single transition is observed if $R_{EE} > d$. A simple interpretation of this is that, for $R_{EE} > d$, the distinction between the surface and the bulk of the film becomes impossible to make and a single transition is expected accordingly. All these results are part of a more comprehensive study of glass transitions in conjugated polymer thin films including PFO which is underway and will be published elsewhere.

In closing, we have shown that polarized Raman spectroscopy can be used to monitor $T_g$ in thin polymer films. The technique is validated by using the widely studied polymer PS. We hope our experimental demonstration here, that changes in phase transition temperatures

can be monitored with RS (and that they give information on the glass transition of thin films in situations where other experimental techniques might be very difficult or impossible) will encourage further work along these lines.

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