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Abstract. Measurements of the dielectric constant of poly(n-butyl acrylate) have been taken in the frequency range 100 Hz–3 GHz, for temperatures between 254 and 359 K. Analysis of dielectric data and their comparison with results recently obtained on the same system by Brillouin light scattering have evidenced a two-step relaxation process. Dielectric spectra account for the behaviour of the slower process, i.e. the structural relaxation, while Brillouin spectra are particularly sensitive to the faster process, i.e. the secondary relaxation. The temperature behaviour of these processes is not in accordance with the predictions of the mode-coupling theory, while it can be suitably interpreted by a model that relates the high-frequency dependence of the dielectric loss curve to the local chain dynamics and the low-frequency dependence to the intermolecular correlation.

1. Introduction

The relaxation of liquids and polymer melts near the glass transition is a quite complex process, whose microscopic description is still an open problem in condensed-matter physics [1]. Although a comprehensive model does not exist, considerable progress has been recently achieved by theories describing the dynamics of these systems above the glass transition temperature (T_g) [2,3]. The mode-coupling theory (MCT) [4] deals with the dynamics of fragile [5] glass forming simple liquids in the frequency window between about 1 MHz and 1 THz. One of the central predictions of this theory is the temperature independence of the shape of the structural relaxation (time–temperature scaling law) above a crossover temperature T_c typically located 40–50 K above T_g. For temperatures approaching T_g, the MCT is no longer suitable for studying the behaviour of the structural relaxation. Qualitative and quantitative predictions in this temperature region are made by the models proposed by Campbell and co-workers [6] and by Schönhals and co-workers [7, 8].

Campbell and co-workers predict a broadening of the structural relaxation due to changes in the morphology of the configuration space. According to their model, for decreasing temperatures an increasing portion of the configuration space becomes energetically inaccessible to diffusion, so the structural relaxation is no longer described by a simple exponential law but by a stretched exponential $\exp[-(t/\tau)^{\beta_K}]$. One single parameter, i.e. the stretching exponent β_K, accounts for the shape of the relaxation function; its value decreases from $\beta_K = 1$ (Debye relaxation) to the $\beta_K = \frac{1}{3}$ for temperatures decreasing toward T_g.

Schönhals and co-workers relate the broadening of the low- and high-frequency regions of the structural relaxation to intermolecular interaction and to hindrance in local chain diffusion respectively. As opposed to Campbell's model, two shape parameters are thus

required to describe the relaxation, one relating to the low- and the other to the high-frequency part of the relaxation function. Moreover the Debye relaxation regime is never expected in polymeric systems because of hindrance in local chain diffusion which also persists at high temperatures.

The predictions of these theories have been recently verified on both simple and polymeric glass-forming systems [2–4, 9–11]. To this respect, we notice that the MCT was developed for simple systems, so its applicability to the dynamics of complex systems, such as polymeric melts, is still open to controversy. Moreover, it is still not clear whether the stretched-exponential law is universally suitable for describing the structural relaxation for temperatures approaching T_g [7, 12]. For these reasons, a careful experimental investigation of the dynamics of polymeric systems near the glass transition has been strongly suggested [4].

In this paper we analyse the relaxation behaviour of the polymeric glass forming system poly(n-butyl acrylate) p(BA) by means of both broad-band dielectric spectroscopy and Brillouin light scattering [13]. The temperature behaviour of the structural and secondary relaxations is reported and quantitatively compared with the predictions of the above theories. In particular, the occurrence of an overlapping of relaxation processes and the validity of the time–temperature scaling law predicted by the MCT is tested by analysing the temperature dependence of the relaxation parameters up to temperatures 150 K higher than T_g. Moreover, the behaviour of the structural relaxation shape parameters for temperatures approaching T_g is discussed in terms of the theories proposed by Campbell and co-workers and by Schönhals and co-workers.

2. Experiments and results

Commercial grade p(BA) in toluene solution, provided by Aldrich Chimica, was employed without further purification; the solvent was pumped out directly from the measuring cell. The calorimetrically defined glass transition temperature is 203 K [14].
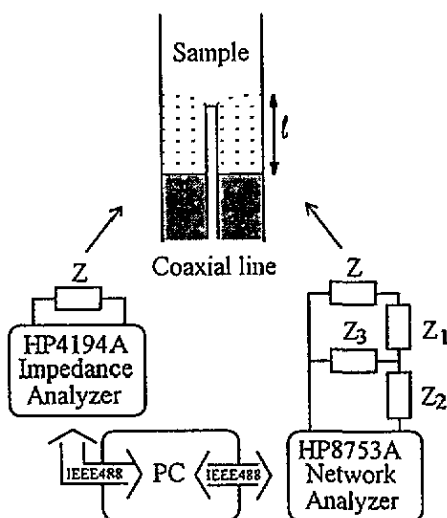

Figure 1. A block diagram of the experimental set-up.

Dielectric measurements were performed over seven decades of frequency by using two different techniques (see figure 1). In the low-frequency interval (100 Hz–40 MHz) the impedance of a cylindrical condenser cell was measured by means of the impedance analyser HP 4194A; in the high-frequency interval (10 MHz–3 GHz), the reflection coefficient of a transmission line terminated by an open coaxial cell was measured by means of the network analyser HP 8753A. The temperature was varied in the interval 254–359 K and controlled within 0.1 K by means of a liquid flow provided by a thermostatic bath.
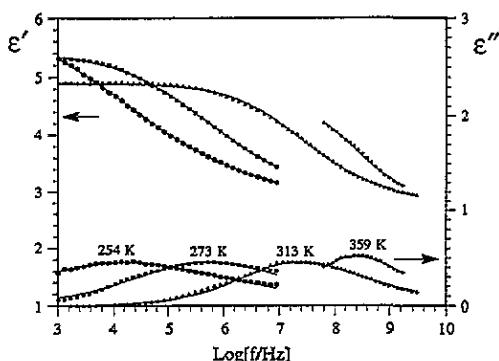

Figure 2. ε' and ε'' of p(BA) versus frequency at different temperatures (points are experimental values; solid lines are the HN fitting curves).
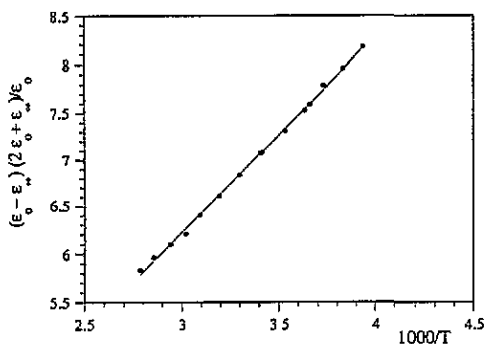

Figure 3. The temperature dependence of $[\varepsilon_0 - \varepsilon_\infty][2\varepsilon_0 + \varepsilon_\infty]/\varepsilon_0$. The values of ε_0 are taken from table 1, while ε_∞ has been determined by a best-fit procedure. T is expressed in kelvin.

Dielectric measurements were performed as a function of frequency at 14 different temperatures; the real (ε') and imaginary (ε'') parts of the dielectric constant relating to four temperatures are plotted in figure 2. The dielectric spectra show the existence of a broad relaxation, which shifts toward lower frequencies as temperature decreases. The main contribution to this relaxation process originates from the orientation of the molecular charge distribution, which has a dipolar term lying on the (CO)–O group of the side chain. This can be identified as the structural relaxation since the value of the apparent activation energy near T_g is higher than the dissociation energy of the C–C bond, thus confirming its cooperative

nature. No secondary relaxation is seen in the dielectric spectra and the structural relaxation is properly described by a single Havriliak–Negami (HN) [15, 16] equation:

$$[\varepsilon^*(\omega) - \varepsilon_1]/(\varepsilon_0 - \varepsilon_1) = 1/[1 + (i\omega\tau)^{1-\alpha}]^\beta \tag{1}$$

where ε_0 is the relaxed dielectric constant, ε_1 the unrelaxed dielectric constant, τ the relaxation time and α and β are shape parameters. We notice that the HN function is particularly appropriate to extract the relevant relaxation parameters to be compared with the above-mentioned theories on the dynamics of glass-forming systems. In fact, (i) the high- ($\omega \gg 1/\tau$) and low- ($\omega \ll 1/\tau$) frequency limits of (1) are the power laws $\varepsilon''(\omega) \sim \omega^{-n}$ and $\varepsilon''(\omega) \sim \omega^m$, predicted by the model of Schönhals and Schlosser [8], the scaling parameters m and n being related to α and β through the relations $m = 1 - \alpha$ and $n = (1 - \alpha)\beta$, (ii) the high-frequency power law also coincides with the so called von Schweider power law predicted by the MCT for the high-frequency, high-temperature tail of the structural relaxation [4] and (iii) in the high-frequency limit, the parameter n coincides with the stretching parameter β_K entering into the Campbell theory [6]; more generally the HN relaxation function, with a proper choice of the parameters α and β, provides, in the frequency domain, a good approximation to the Fourier transform of the stretched exponential law [17, 18].

Table 1. Dielectric parameters of p(BA) at different temperatures.

T (K)	ε_0	ε_1	τ (s)	$1 - \alpha$	β
254	5.62	2.75	1.95×10^{-5}	0.36	0.77
261	5.52	2.75	5.70×10^{-6}	0.39	0.78
268	5.44	2.75	1.42×10^{-6}	0.46	0.66
273	5.35	2.75	6.58×10^{-7}	0.48	0.68
275	5.32	2.75	4.98×10^{-7}	0.48	0.68
283	5.22	2.75	1.94×10^{-7}	0.51	0.66
293	5.12	2.75	7.35×10^{-8}	0.55	0.65
303	5.01	2.75	3.48×10^{-8}	0.58	0.61
313	4.91	2.70	1.50×10^{-8}	0.60	0.60
323	4.81	2.70	8.32×10^{-9}	0.65	0.58
331	4.72	2.69	3.33×10^{-9}	0.70	0.59
340	4.67	2.68	2.36×10^{-9}	0.73	0.58
350	4.61	2.63	1.99×10^{-9}	0.75	0.55
359	4.55	2.60	1.33×10^{-9}	0.77	0.54

The dielectric spectra have been thus fitted by (1). The parameters obtained at different temperatures are reported in table 1 and the curves corresponding to these parameters are shown in figure 2 as full lines.

The temperature behaviour of ε_0 is consistent with that predicted by the Kirkwood–Froelich equation [19], which can be written in terms of the static correlation function of the total dipole M of a spherical domain of volume V as

$$[\varepsilon_0 - \varepsilon_\infty][2\varepsilon_0 + \varepsilon_\infty]/\varepsilon_0 = (4\pi/KT)\langle M(0)M(0)\rangle/V \tag{2}$$

where ε_∞ is the dielectric constant at optical frequencies. In principle, both $\langle M(0)M(0)\rangle$ and V can be temperature dependent since the correlation function implicitly contains the short-range interactions between molecules, and V can be affected by the temperature dependence of the mass density. However, for the temperature range considered here,
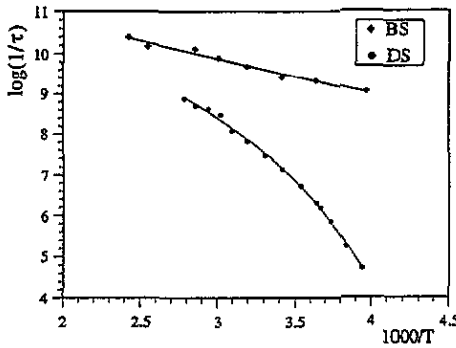
Figure 4. An Arrhenius plot of the relaxation time τ determined from dielectric spectroscopy and Brillouin scattering experiments. T is expressed in kelvin.

these effects are negligible, as shown in figure 3 by the fairly good agreement between the experimental data and the fitted curve. From the fitting procedure it was possible to obtain the value $\varepsilon_\infty = 2.2$, corresponding to a refractive index $n = \varepsilon_\infty^{1/2} = 1.48$, which is consistent with that obtained by previous BS measurements [13]. Moreover, we notice that the values of the unrelaxed dielectric constant ε_1 reported in table 1 are higher than that of ε_∞, in agreement with the existence of a secondary relaxation process located out of the present dielectric frequency window [20].

As for the temperature dependence of the structural relaxation time, the values of $\tau(T)$ reported in table 1 have been fitted by the Vogel–Fulcher equation:

$$\tau(T) = \tau_0 \exp(DT_0/(T - T_0)) \tag{3}$$

where T_0 is the Kauzmann temperature and D is a parameter typically ranging between three and 100, depending on the fragility of the system [5]. Figure 4 shows the experimental data and the curve obtained by the best-fit procedure, which gives the following values: $\tau_0 = 1.0 \pm 0.5$ ps, $T_0 = 178 \pm 7$ K and $D = 7.2 \pm 1.3$. Because of the low value of D and of the observed non-exponential (non-Debye) behaviour of the structural relaxation, p(BA) can be included among fragile systems.
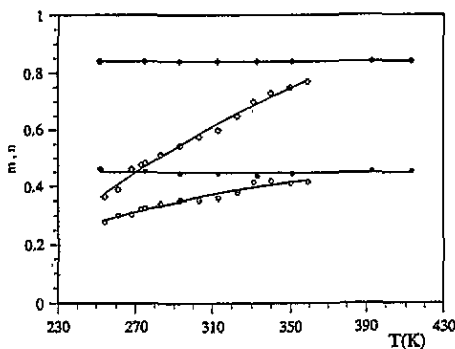

Figure 5. The scaling parameters m and n versus T determined by Brillouin ($\blacklozenge$, m; $\bullet$, n) and dielectric ($\Diamond$, m; $\bigcirc$, n) measurements.

The temperature dependence of the shape parameters is shown in figure 5. We have preferred to represent the behaviour of m and n rather than α and β in order to achieve a direct comparison with the predictions of the theories.

3. Discussion

A more thorough understanding of the dynamics of p(BA) can be obtained by comparing the dielectric data presented above with those recently obtained on the same system by BS measurements performed in the frequency region 1–20 GHz and for temperature ranges between 170 K and 460 K [13]. In that paper, the influence of relaxation processes on the propagation of longitudinal acoustic waves was described by the complex, frequency-dependent, longitudinal acoustic modulus $M^*(\omega) = M'(\omega) + iM''(\omega)$ [21], which was expressed in terms of an HN function. For a comparison of BS results with dielectric data, the values of the relaxation parameters obtained by fitting BS spectra at different temperatures are here expressed in the susceptibility formalism [14]. To this end, the reciprocal of the values of $M^*(\omega)$ obtained by BS have been fitted to an HN function. The values obtained for the relaxation times and for the shape parameters are shown in figures 4 and 5, respectively, together with those relating to dielectric data. We notice that the temperature behaviour of the BS relaxation time reported in the Arrhenius plot of figure 4 is quite distinct from that of the DS data, showing an Arrhenius behaviour characterized by a low value of the activation energy, which is typical of secondary relaxations. The same feature was also observed in previous BS studies of liquids, including polymers, near the glass transition [22–26]. The discrepancy between BS and DS data indicates that, even if BS is sensitive to density fluctuations and can, in principle, be applied to the study of the structural relaxation [4], it may happen that the contribution (relaxation strength) of secondary relaxations becomes dominant in the BS frequency window, thus masking the structural relaxation. The existence of a secondary relaxation in p(BA) has been recently evidenced by dielectric measurements performed at temperatures lower than T_g [27]. We notice that for $T > T_g$ this relaxation is located out of the present dielectric frequency window so that it can only be studied through BS data. The above considerations permit us to discuss in more details the experimental results, distinguishing the high-temperature from the low-temperature regimes as follows.

(i) At high temperatures, the parameters m and n relating to the main and secondary relaxation phenomena tend to overlap (figure 5). In the same temperature region the apparent activation energies become comparable, while the relaxation times measured by the two techniques are at least one decade apart (see figure 4). In the framework of MCT, this feature can be explained by recalling that Brillouin and dielectric data refer to the dynamics of different microscopic variables. For temperatures higher than a critical temperature T_c an 'α-scale universality' holds, such that the relaxation time τ_A of a microscopic variable A is proportional to a universal function $f(T)$ through a temperature-independent factor C_A [4, 28]. This factor can be responsible for the vertical shift in the Arrhenius plot of relaxation times relative to Brillouin and dielectric data so that, in the framework of the MCT, it is more consistent to consider the slope of $\tau(T)$, i.e. the apparent activation energies, rather than the absolute value of $\tau(T)$ itself. In the present case, dielectric and Brillouin activation energies tend to become mutually comparable for $1000/T < 2.8$ (figure 4), corresponding to $T > 1.78T_g$; also the parameters m and n relating to DS and BS tend to coincide in this same region, thus suggesting that a collapse of structural and secondary relaxation processes occurs for $T > 1.78T_g$. As for the value of n, this parameter, which accounts for the shape of the high-frequency part of the structural relaxation, is temperature dependent in almost

all the range analysed. This means that a time–temperature scaling law does not hold up to very high temperatures (figure 5). It follows that both the collapse of relaxation processes and the validity of a time–temperature scaling law does not occur up to $T > 1.78T_g$, so it is not possible to identify the presence of a critical temperature in the sense of MCT in the whole temperature range analysed. We note that, in contrast to the present results, both the collapse and the validity of the scaling law for systems in which the MCT was successfully applied starts to hold in a narrow temperature region located between $1.2T_g$ and $1.28T_g$ [4, 9, 29].

(ii) For decreasing temperatures, the behaviour of both $m(T)$ and $n(T)$ partially agrees with the predictions of the theory of Campbell and co-workers [6], since the stretching increases and the parameter n approaches the value $\frac{1}{3}$ predicted by the theory. However, if both the high- and the low-frequency parts of the structural relaxation are considered, the values of m and n do not correspond to a well defined value of the stretching parameter β_K [17, 18]. This means that in p(BA) the stretched exponential function is not appropriate to describe the whole structural relaxation function. Moreover, the value $m = n = 1$ (Debye relaxation), predicted by the theory in the high-temperature limit, is never attained by our experimental results. The model proposed by Schönhals and co-workers [7, 8, 16], on the other hand, seems to be more appropriate to describe the behaviour of p(BA) relaxation. This model is based on the scaling hypothesis that the characteristic time of a movement is proportional to its spatial extent, so the shape of the dielectric loss curve depends on the local chain dynamics at high frequencies ($\omega \gg 1/\tau$) and on the intermolecular correlations at low frequencies ($\omega \ll 1/\tau$). The parameter n is thus related to the local chain dynamics, i.e. to the intramolecular correlation, while m is related to the degree of intermolecular correlation. The observed decrease of the values of the scaling parameters for temperatures approaching the glass transition can thus be related to an increase of both intermolecular interaction and hindrance in the polymer chain local diffusion. The upper limiting value $m = n = 1$ is expected only for low-molecular-weight systems, whose local diffusion is scarcely hindered, thus admitting a Debye relaxation. In the case of polymeric systems, the hindrance in local chain motion leads to a limiting value $n = 0.5$, consistent with our experimental results.

In summary, the HN relaxation function has shown to be appropriate to fit the frequency behaviour of both the real and the imaginary part of the measured dielectric constant of p(BA). The temperature dependence of the structural relaxation time is suitably described by a Vogel–Fulcher equation in the whole temperature range analysed. As for the shape parameters, they are temperature dependent, i.e. a time–temperature scaling law does not hold up to temperatures higher than $1.78T_g$. The temperature behaviour of these parameters is consistent with the model proposed by Schönhals and Schlosser which relates the decrease of their values with decreasing temperature to the increase of both intermolecular interaction and hindrance in the polymer chain local diffusion [8]. At high temperatures the values of these parameters become comparable with those deduced by BS measurements in a previous investigation [13]. These results, together with the Arrhenius behaviour of the relaxation time obtained by BS, have been interpreted as the occurrence of a two-step relaxation process, collapsing into a single relaxation at temperatures higher than $1.78T_g$. Both the collapse of the relaxation processes and the validity of a time–temperature scaling law are thus located at temperatures much higher than those typical of the glass-forming systems for which an MCT analysis was successfully performed [4, 9, 29].

Acknowledgment

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