Colloid Polym Sci 273:413–420 (1995)
© Steinkopff Verlag 1995

ORIGINAL CONTRIBUTION

B. Frick
U. Buchenau
D. Richter

Boson peak and fast relaxation process near the glass transition in polystyrene

Received: 12 July 1994
Accepted: 6 September 1994

Dr. B. Frick (✉)
Institut Laue Langevin
Avenue des Martyrs
BP 156X
38042 Grenoble, France

U. Buchenau · D. Richter
Institut für Festkörperforschung
Forschungszentrum Jülich
52425 Jülich, FRG

Abstract Atactic polystyrene, both side group and main chain deuterated, was investigated by inelastic neutron scattering in a wide temperature range around the glass transition from 2 to 450 K. In the glass the Boson peak position is only very weakly influenced by the deuteration of the phenyl group. In the neighborhood of the glass transition temperature T_g we find a fast relaxation process similar to other glasses. The onset of the fast relaxation in polystyrene, however, is observed already at temperatures $T_g - 200$ K. Results from partially deuterated polystyrene suggest a change of the phenyl ring dynamics already far below T_g.

Key words Polymers – glass transition – neutron scattering – polystyrene

Introduction

The origin of the Boson peak which is observed by inelastic neutron scattering or by Raman scattering [1, 2] in amorphous systems as an excess vibrational scattering over the expected Debye contribution is still unclear. Another unexplained fact is the experimental observation of a fast relaxation process in glasses near the glass transition temperature, interpreted as a fast β-relaxation by the mode-coupling theory [3]. Alternatively, the fast process is interpreted in close connection to the soft potential model [4] and it is proposed that the fast relaxation might be related to the well known low temperature anomalies of amorphous systems in the specific heat and the thermal conductivity. Certainly the understanding of these effects is one major goal in solid-state physics today.

In the past, neutron and Raman scattering experiments could show that the above-mentioned phenomena are intrinsic for glasses and are not due to side group relaxation effects in polymers [1, 2]. Generally, the low-frequency scattering which arises in most samples with increasing temperature near T_g and below the Boson peak position leads at higher temperatures to an overdamping of the Boson peak (i.e., to a quasielastic spectrum). In most cases the overdamping is observed above T_g. We report here on inelastic neutron scattering data from atactic polystyrene (PS; $T_g = 375$ K) for which, like for polycarbonate [5], the onset of the fast relaxation process was recently reported to occur already below T_g [5].

Furthermore, a drastic isotope effect in the peak position was reported for polystyrene [6]. This information was deduced from the difference scattering of fully protonated PS and phenyl ring deuterated PS. Such a procedure can give only an approximate idea of the backbone relaxation and we therefore study PS-d3 directly. An influence of the isotope substitution onto the Boson peak could contribute to the understanding of its origin.

Here, we present a set of temperature-dependent inelastic neutron scattering data using three different spectrometers and differently labeled polystyrene. To a certain extent this allows us to get information on the side group and main chain dynamics for times shorter than several picoseconds and for temperatures covering the glass and the melt of polystyrene. We will discuss our data comparing them to known experimental results from neutron scattering [5–10, 20] and to complementary techniques like, e.g., NMR [11–15]. NMR has given a deeper insight into the local phenyl ring dynamics of polystyrene but does not access the same time and momentum transfer regime. The main emphasis of this work is to show how for PS the Boson peak changes with temperature, i.e., gets overdamped already below T_g. The change of the mean squared displacement and these changes appearing in the picosecond time regime for phenyl ring molecules or main chain labeled polymers are presented.

Experimental details

The inelastic neutron spectra on high molecular weight, partially deuterated atactic polystyrenes were recorded on the backscattering spectrometers IN10 and IN13 and on the time-of-flight instrument IN6 at the ILL, Grenoble. The energy resolutions are about $\delta E = 1\ \mu$eV for IN10, $\delta E = 8\ \mu$eV for IN13 and $\delta E = 80\ \mu$eV for IN6. The maxima in energy transfer correspond to 14 μeV, 250 μeV and 100meV (in energy gain) for IN10, IN13, and IN6, respectively. The momentum transfer regime for IN10 and IN6 extends from $Q = 0.2$ Å to $Q = 2.2$ Å and for IN13 from $Q = 0.2$ Å to $Q = 5.2$ Å. The time regimes of these neutron spectrometers are illustrated by the relaxation map [11] for polystyrene in Fig. 1. It shows the α- and secondary relaxations and also that a priori no changes on the neutron time scale would be expected near the glass transition temperature $T_g = 375$ K.

The neutron-scattering data were corrected for background, container scattering and self shielding in the standard way. The measured sample transmissions were about $T = 92\%$ in all cases and therefore multiple scattering corrections were omitted. In the case of time-of-flight (TOF) data the spectra were interpolated to constant Q spectra and normalized to the integral scattering taken between -2 meV and 10 meV. A temperature Bose correction factor was applied to scale these spectra to a common temperature of $T_g = 375$ K.

Results

We will first report on high-energy resolution backscattering experiments for which the temperature dependence of the elastic intensity was investigated. The scattering of PS-d5 is dominated by contributions from the protons of the polymer main chain and the signal remains elastic as long as the relaxation times for these protons are slower than the corresponding instrumental resolution (see Fig. 1). Furthermore, the elastic scattering is weakened with increasing Q and increasing temperature via the Debye–Waller factor DWF = $\exp(-1/3\ Q^2\langle u^2\rangle(T))$. PS-d5 was measured at eight different momentum transfers on IN10. The result for the logarithm of the normalized elas-

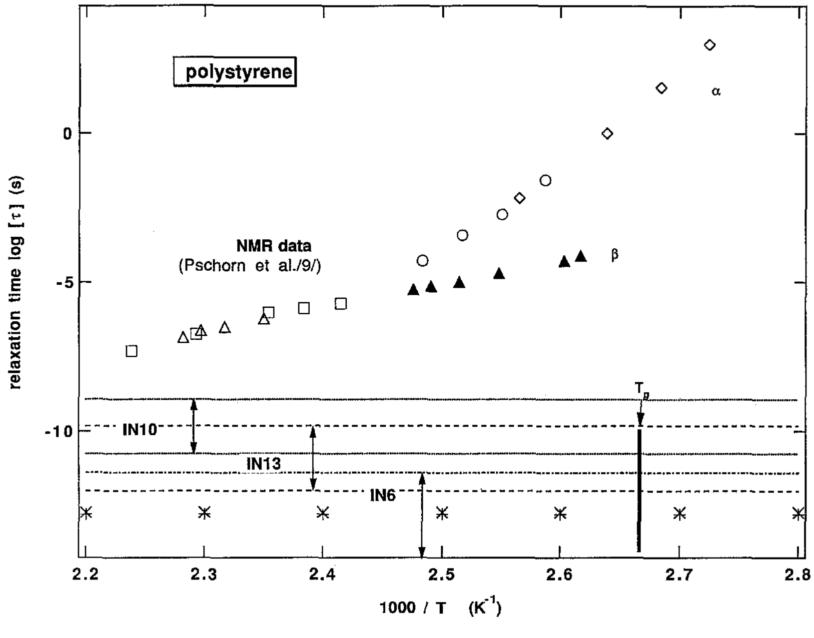


Fig. 1 Relaxation map for polystyrene as determined by different NMR methods [11] (symbols). Lines indicate time scales for the neutron spectrometers, assuming that $\delta E/5$ can be detected. The symbols + and × indicate the measured maxima of the Boson peaks for PS-d3 and PS-d5, respectively

tic scattering is shown in Fig. 2. At the normalization temperature of $T = 4$ K the dynamics is assumed to be frozen. A linear temperature dependence in this representation (solid lines) is expected for harmonic vibrations. All data show clearly a stronger than linear temperature decrease of the elastic scattering above T_g. For momentum transfers of $Q > 0.8$ Å slight deviations from a linear temperature dependence are already observed at temperatures as low as $T = 200$ K.

We have results from measurements on the same sample up to higher Q-values (see Fig. 3; $Q < 5$ Å; 8 μeV resolution; IN13). The lowest temperature measured was $T = 110$ K and therefore it is difficult to extrapolate the scattering intensities towards very low temperatures. But again, one finds a drop of the elastic intensity above 200 K and below the glass transition temperature ($T_g = 375$ K). Both figures indicate that already more than 150 K below T_g some atoms become mobile on the fast time scale of neutron scattering.

Obviously, one would be interested to find out if one can ascribe the observed dynamical changes either to the backbone or to the phenyl rings applying partial deuteration. Unfortunately, we have these particular scans not for PS-d3, but only for PS-h8. Again, these samples were measured on IN10 with exactly the same instrumental configuration like for PS-d5. We show the results for

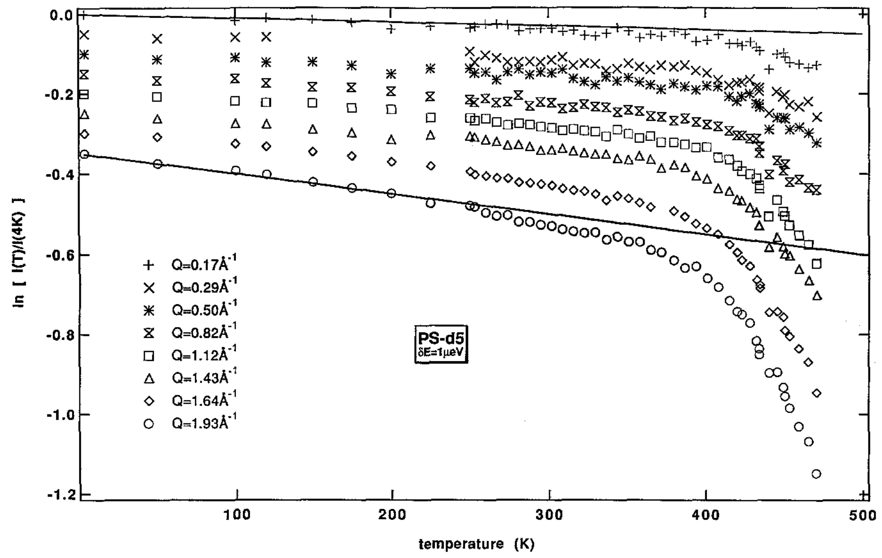


Fig. 2 Elastic scan for PS-d5; IN10 with 1 μeV energy resolution; intensities are normalized to 4 K. The data for different Q-values are shifted by -0.05 against each other for better distinction

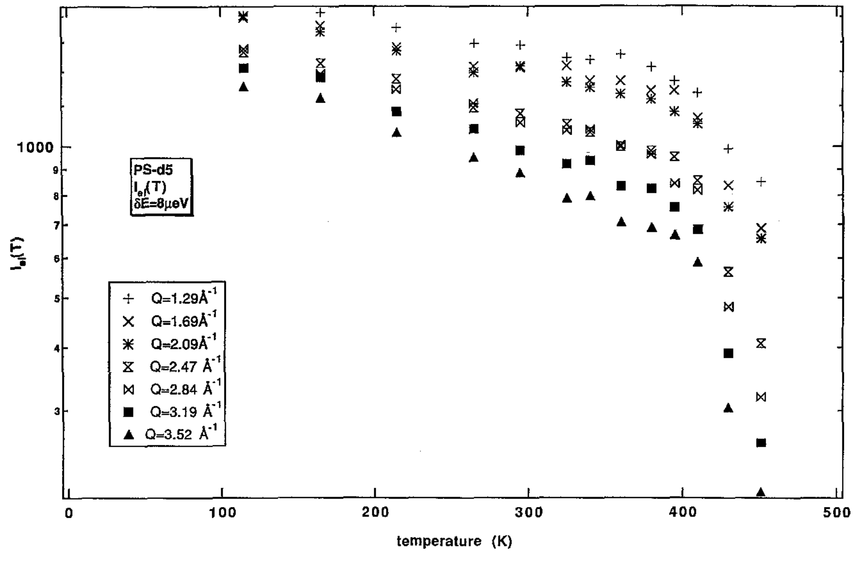


Fig. 3 Elastic scattering of PS-d5 measured on IN13. Intensities are normalized to Vanadium scattering

protonated atactic polystyrene in Fig. 4. The overall features of the elastic scattering of PS-h8 are similar to the results for PS-d5. Again, the data suggest that the intensity decrease sets on below T_g in the temperature region around $T = 150$–200 K. However, for PS-h8 the deviations from a linear temperature decrease are more pronounced than for PS-d5. We take this as an indication for that the phenyl ring motion is involved in this first relaxation process near $T > 150$ K (at $Q = 1.9$ Å^{-1}).

In Fig. 5 these results are summarized by calculating from the previous figures the mean squared displacement $\langle u^2 \rangle(T)$ as a function of temperature. These data result from fitting the Q-dependence of the elastic scattering (Figs. 2–4) and assuming that the elastic intensity decreases with the Debye–Waller factor. The calculated mean squared displacements turns out to be larger above $T = 120$ K for PS-h8 than for PS-d5. Note that the observed intensity in the latter case is dominated by the phenyl ring, whereas it is dominated by the main chain in PS-d5. The dotted line is taken from refs. [5, 6] and is extracted from the elastic scattering of neutron time-of-flight measurements on PS-h8. The agreement with our data is excellent. The data for PS-d5 (∗) taken on IN13 (Fig. 3) and on IN10, respectively, agree well. Thus, we

Fig. 4 Elastic scattering ($\delta E = 1$ μeV) for fully protonated polystyrene PS-h8; the data for different Q-values are shifted by -0.05 against each other

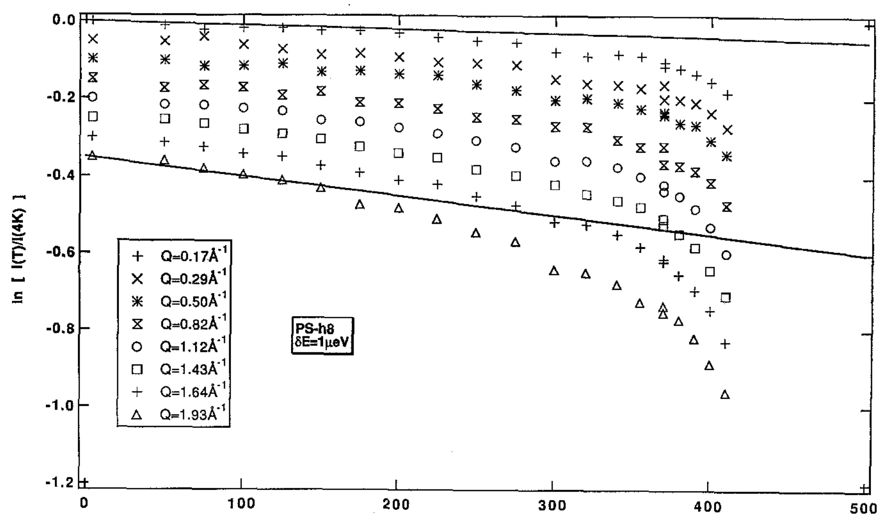
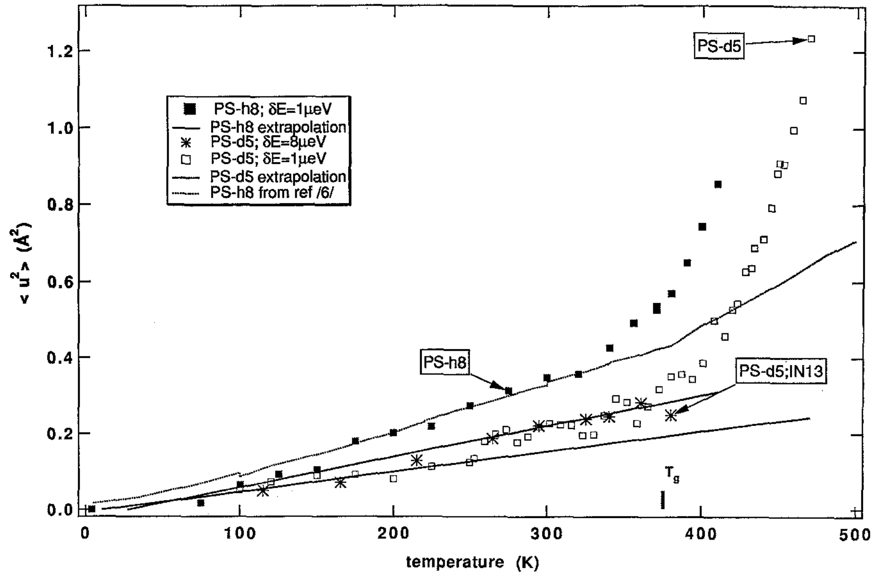


Fig. 5 Mean squared displacements for PS-d5 and PS-h8 (dots) calculated from the Q-dependence of the elastic scattering up to 2 Å^{-1} and with 1 μeV energy resolution from IN10 data. The two straight lines are low temperature extrapolations of the mean squared displacement. Data for PS-d5 measured on IN13 (∗) are shown for comparison

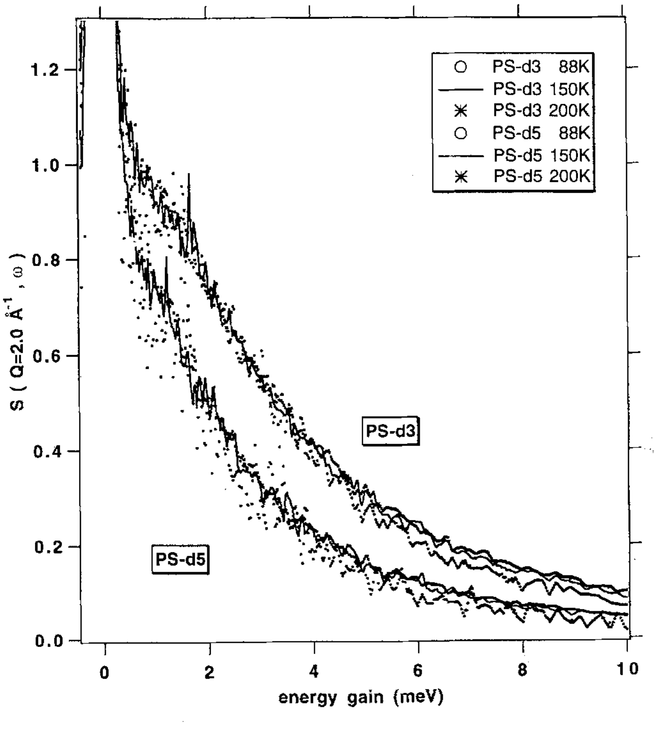


conclude from the elastic scattering and from the study of the Debye–Waller factor of partially deuterated PS that the phenyl ring dynamics begins considerably below T_g.

Now, we turn to the inelastic scattering. The counterpart to the nonlinear decrease of the elastic intensities with increasing temperature is seen mainly in the low frequency region, i.e., below 0.5 THz, as an additional scattering which does not follow the normal Bose factor temperature dependence. We compare in Fig. 6 the spectra for PS-d3 and PS-d5 at $Q = 2\ \text{Å}^{-1}$; the Bose temperature factors of the spectra are scaled to the glass transition temperature and the spectra are normalized as mentioned above. The Boson peak in PS-d3 clearly forms an inelastic shoulder which is located at about 1.5 meV. This shoulder is visible in PS-d5 as well, but it is slightly less pronounced. Within our statistics only a minor effect on the peak position on isotopic substitution is observed. The maximal shift could be of the order of 0.2 meV towards lower energies.

Finally, we show the temperature dependence of the dynamical scattering function for PS-d3 and PS-d5 (Fig. 7a, b). Again the data are corrected as described above. Both figures show that the observed curves can be grouped as: i) a group of low temperature spectra which scale by application of the Bose occupation factor to a common curve (like in Fig. 6), ii) an intermediate group for which weak relaxation is observed in the energy range below 1.5 meV, and iii) a high temperature group of curves which show an overdamped spectrum and again seem to approach a common curve.

Fig. 6 Comparison of the dynamic scattering law of PS-d5 and PS-d3 (measured on IN6, ILL Grenoble). For each sample the scattering laws at 88 K, 150 K and 200 K are shown scaled to $T_g = 375$ K



The first group was discussed above in connection with Fig. 6. The intermediate group shows a weak onset of low frequency scattering which does not follow the Bose factor scaling below 1.5 meV. This observation holds for both samples, but is more pronounced for PS-d3 than for PS-d5. The temperature regime in which the onset of low frequency scattering is observed corresponds to the same temperature regime for which the elastic scattering in Figs. 2–4 starts to drop. Thus we find another indication for the importance of the phenyl ring dynamics in this temperature range.

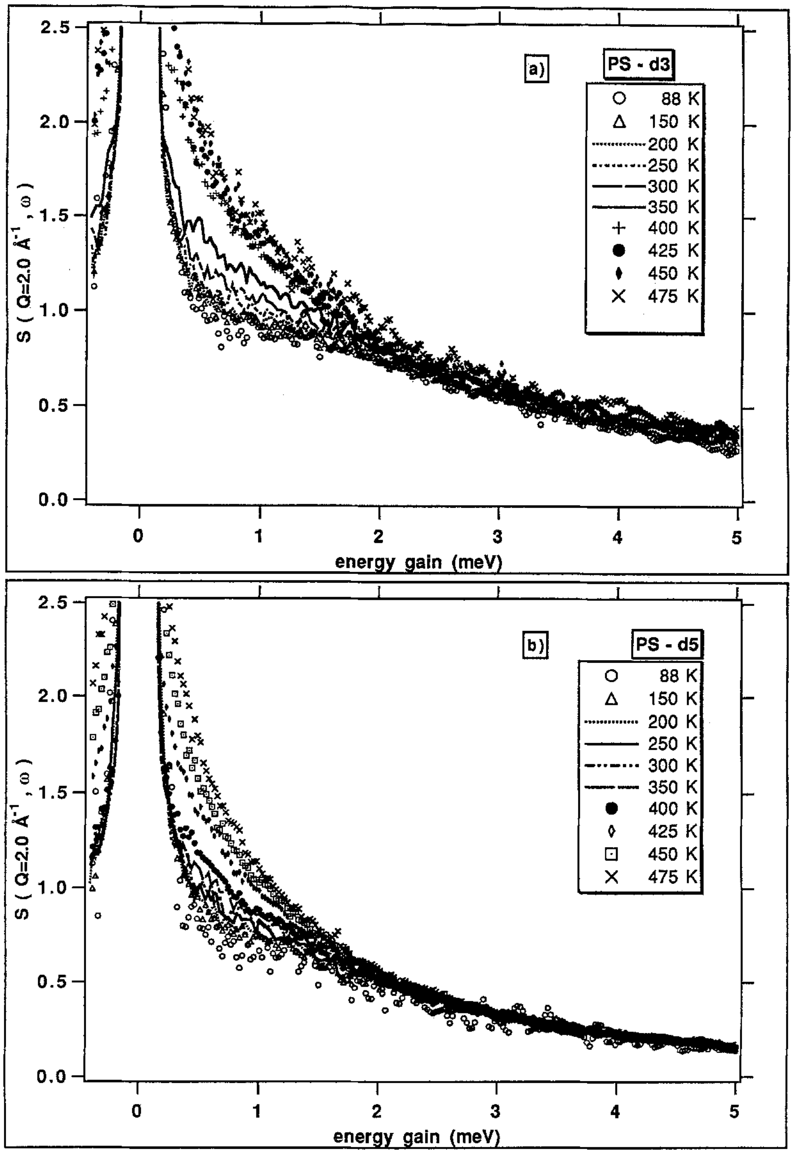
The last group of curves for temperatures $T > T_g = 375$ K presents quasi- elastic spectra in the frequency range below 5 meV, which undergo with further temperature increase only minor changes. For PS-d5 there is a slightly stronger temperature dependence than for PS-d3 and the most pronounced difference is the 400 K spectrum, which shows much less low frequency scattering for PS-d5 than for PS-d3.

Discussion

From the presented data it is clear that the dynamic behavior of the protons of the phenyl ring is different from the dynamics of the backbone protons. We will separate the discussion into two distinct parts, namely the behavior at low temperatures and the behavior at higher temperatures.

Let us first discuss the low temperature case. The low temperature relaxation is more pronounced for samples having protonated phenyl rings (PS-d3, PS-h8). Our data do not allow to draw conclusions about the type of phenyl ring motion which might be involved. A possible phenyl ring flip should produce a minimum in the elastic incoherent structure factor at about 3 Å (only PS-d5 was measured up to such high Q-values), but from NMR experiments the dynamics of such π-flips is expected to be much slower [12, 13] (see Fig. 1). On the other hand, for normal harmonic vibrations we would expect a Q-dependence of $\ln(I_{el})$ versus Q^2 which is linear and our data show deviations from such a behavior, especially at the higher Q-values. This might indicate the onset of some type of molecular motion, librations, anharmonic vibrations. Temperature-dependent changes of the static coherent structure factor contributions [17] would lead to a redistribution of intensities in the observed Q-range and not to a general drop. Quasielastic measurements on both IN10

Fig. 7 Temperature dependence of the normalized inelastic spectra of a) PS-d3 at 2 Å. b) Temperature dependence of the normalized inelastic spectra of PS-d5 at 2 Å



and IN13 could not reveal any broadening of the elastic line below T_g for PS-h8 and PS-d5. This agrees with inelastic neutron scattering results by Zajac et al. [10] on PS-h8 with somewhat worse resolution than on IN10. For PS-d3, Zajac et al. find no broadening of the elastic signal at all. For the PS-d5, Zajac et al. describe their data taking a very weak quasielastic component with a half-width of about 17 μeV at room temperature into account. In fact, this additional intensity might be caused by contributions outside their spectral window and which we detect on IN6 (Fig. 7) in the inelastic or quasielastic region below 1 meV.

We propose that the oscillation or librational amplitudes of the phenyl rings might become rather large with increasing temperature already below T_g and eventually might be coupled to the main chain. This would be in agreement with the phenyl ring flips which have been detected on the slower NMR time scale [12, 13], which were found to be coupled to the main chain motion [10, 11] and which have evidenced a strong motional heterogeneity [11]. We have recently found indications for such a local heterogeneity in the case of the methyl group dynamics in amorphous polyisoprene [18]. A broad distribution of activation energies or relaxation times had to be assumed in order to explain a slow decrease of the elastic intensity. For PS, mechanical experiments by Yano et al. [16] have been interpreted assuming the existence of phenyl ring flips as well.

The second dynamic process sets in near to the glass transition temperature. It is clear by now that this relaxation process is intrinsic for very different type of glasses near T_g and that it is not due to side-group dynamics only. The onset temperature is in some cases, like for the main chain polymer polybutadiene, weakly observable far below T_g. For polystyrene, due to the phenyl ring dynamics its exact onset temperature is not easy to define. The determination of the onset temperature will depend strongly on the open question whether the relaxation process observed above T_g is strictly different from below T_g. Thus, the dynamic structure factor should be known with high precision. Phenyl ring librations and flips coupled to the main chain motion might well be the "elementary process" of more extended modes above T_g. Neutron scattering data for the elastic incoherent structure factor of poly(methylstyrene) [9] above T_g were interpreted as being due to phenyl ring π-flips and thus were brought into connection with the fast β-relaxation process. Such a conclusion seems not to be evident for polystyrene, but rather the phenyl ring dynamics sets on already far below T_g, most probably involving librations of the rings. On the other hand, our data do not access high enough Q values to extract a meaningful formfactor for such flips and to clarify their contribution to the fast process. Nevertheless, the results from main chain polymers [19] and low molecular glasses leave no doubt that the phenyl ring dynamics is not essential for the appearance of this fast process.

Are there arguments in favor of the proposition that the fast relaxation observed between $T = 150$ K and T_g might be the same as the fast process found close to T_g [5]? We have discussed how our results from the partially deuterated polystyrenes rather support the idea that the phenyl ring dynamics changes in the low temperature range. First, we can not completely exclude that this might be a precursor of the fast process appearing close to T_g. Secondly, for PS-d3 the main changes of the spectra appear for temperatures below the glass transition (Fig. 7a), wheras there are only minor changes for temperatures higher than $T = 400$ K. The complementary deuteration for PS-d5 does not have a pronounced effect on the Boson peak position, but has a considerable effect on the increase of the low frequency scattering with increasing temperature. Above T_g for PS-d5 there are more pronounced changes at frequencies lower than the Boson peak maximum than for PS-d3. Thus, we might as well conclude that the differences between PS-d3 and PS-d5 in Fig. 7 are based on a retarded relaxation of PS-d5, the sample which contains the heavier phenyl rings. We do not have clear experimental evidence against such a view. Let us also mention that inelastic neutron scattering experiments on selectively deuterated glycerol have given different Debye Waller factors for the hydrogens of the center molecule and for the hydrogens participating in the hydrogen bonding between different molecules. This was explained by their difference towards the center of mass of the molecule [20]. Following this interpretation we would have to assume for PS librations of the phenyl ring around the backbone axis in addition to librations around the ring flip axis. Again, this could be related to the fast relaxation process which is in glasses usually observed only above T_g.

In conclusion, our measurements confirm the onset of a fast relaxation process in polystyrene at temperatures far below the glass transition temperature. From partial deuteration we find that the phenyl ring dynamics, probably ring librations, are involved in this process below T_g. Close to T_g, we observe the usual upturn of the mean squared displacement and observe the corresponding low frequency scattering of the fast process. The latter is more pronounced for PS-d5, the sample with stronger scattering from the main chain. The very strong breakdown of the elastic scattering above 400 K and the corresponding drastic increase of the mean squared displacement are due to the much slower α-relaxation, which was not investigated in this work.

References

1. See e.g. Richter D, Dianoux AJ, Petry W, Texeira J (eds) (1989) In: 'Dynamics of Disordered Materials'. Springer Proceedings in Physics 37, Springer Verlag, Berlin; or Dianoux AJ, Petry W, Richter D (eds) (1993) In: 'Dynamics of Disordered Materials II'. Physica A, Vol 201; North-Holland, Amsterdam
2. Sokolov AP, Rössler E, Kisliuk A, Quitmann D (1993) Phys Rev Lett 71:2062
3. Götze W (1991) In: 'Liquids, Freezing and the Glass Transition'; Hansen JP, Levesque D, Zinn-Justin J (eds); North-Holland, Amsterdam; p.287
4. Buchenau U, Galperin YuM, Gurevich VL, Parshin D, Ramos M, Schober HR (1992) Phys Rev B 46:2798
5. Buchenau U (1994) Journal of Non-Crystalline Solids 172–174:391; Kanaya T, Kawaguchi T, Kaji K (1994) ibidem:327; Buchenau U, Schönfeld C, Richter D, Kanaya T, Kaji K, Wehrmann R (1994) Phys Rev Lett 73:2344
6. Kanaya T, Kaji K, Inoue K (1992) Physica 180&181:814
7. Linder K (1993) Diplomarbeit Forschungsanlage Jülich
8. Linder K, Frick B, Buchenau U (1993) Physica A 201:112
9. Meier G, Fujara F, Petry W (1989) Macromolecules 22:4421
10. Zajac W, Gabrys B, Pfeiffer DG, Adams MA (1992) Physica B 182:365
11. Pschorn U, Rössler E, Sillescu H, Kaufmann S, Schaefer D, Spiess HW (1991) Macromolecules 24:398
12. Spiess HW (1983) Colloid Polym Sci 261:193

Colloid & Polymer Science, Vol. 273, No. 5 (1995)

13. Lindner P, Rössler E, Sillescu H (1981) Macromol Chem 182:3653
14. Sillescu H (1981) In: 'IUPAC Macromolecules'; Benoit H, Rempp P (eds); Pergamon Press: Oxford, p 155
15. Sillescu H (1986) Makromol Chem Macromol Symp 1:39
16. Yano O, Wada Y (1971) J Polym Sci Pol Phys Ed 9:669
17. Gabrys B, Schärpf O (1992) Physica B 180&181:495
18. Frick B, Fetters L (1994) Macromolecules 27:974
19. Frick B, Richter D, Petry W, Buchenau U (1988) Z Phys B 70:73; and Frick B, Richter D (1989) in ref [1]:37:38
20. Fujara F, Petry W, Diehl RM, Schnauss W, Sillescu H (1991) Europhys Lett 14:563