Local Dynamics of Some Bulk Polymers above T_g As Seen by Quasielastic Neutron Scattering

T. Kanaya,* T. Kawaguchi, and K. Kaji

Institute for Chemical Research, Kyoto University, Uji, Kyoto-fu 611, Japan

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ABSTRACT: Quasielastic neutron scattering experiments have been performed on polyisobutylene, *trans*-1,4-polychloroprene, and polyethylene in the energy range from 0.01 to 10 meV at temperatures far above the glass transition temperature T_g and on *cis*-1,4-polybutadiene near T_g. Similar to the previously reported results on *cis*-1,4-polybutadiene far above T_g, we observe in these polymers a slow process on a time scale from several tens to several hundreds of picoseconds which we term the E-process (or elementary process) as well as a fast process with a time scale of about a picosecond. We consider the relaxation time map of polybutadiene near and above the glass transition temperature to illustrate that the fast process is common for most glass-forming materials and that the E-process may be assigned to an elementary process involving local chain conformational transitions. Finally, we analyze the E-process in terms of a previously introduced jump diffusion model with damped vibrations, which is consistent with recent results of molecular dynamics simulations for bulk amorphous polymers, and we discuss the possible mechanism of the conformational transitions.

1. Introduction

Extensive theoretical and experimental work has been carried out on local dynamics of polymers in solution and bulk to elucidate the mechanism of conformational transitions.[1] Previously, it was believed that the most reasonable mechanism for the conformational transitions was a crankshaft-like motion such as the Schatzki crankshaft[2] or three-bond motions[3] in which two bonds in a main chain rotate simultaneously. However, computer simulations on isolated chains[4,5] have shown that single-bond rotations occur frequently in polymer chains along with counterrotations of two second-neighboring bonds separated by a trans bond. These simulations also showed that the apparent activation energy of a conformational transition is approximately equal to the energy barrier of a single C−C bond rotation. In a previous paper,[6] we performed quasielastic neutron scattering (QENS) measurements on *cis*-1,4-polybutadiene (PB) far above T_g and analyzed the data in terms of a jump diffusion model with damped vibrations, which approximately has the same physical picture as the results of the computer simulations although these were made on isolated chains. Recently, computer simulations have been performed on bulk amorphous polymers,[7−13] indicating that the mechanisms of the conformational transitions are surprisingly similar to those of isolated chains. As these results are consistent with our previous work on PB and the model used in that work, we have decided to extend our QENS study to other polymers with different chemical structure. In this work, therefore, we have extended quasielastic neutron scattering measurements to three other polymers—polyisobutylene (PIB), *trans*-1,4-polychloroprene (PCP), and polyethylene (PE)—to confirm whether the physical picture predicted by the computer simulations also holds for these polymers.

Alternatively, the dynamics of bulk amorphous polymers have been extensively studied from the viewpoint of the dynamics of glass-forming materials, including polymers, organic, and inorganic glass-forming materials.[14−16] Experimental studies using many different techniques have revealed that the α-process, the Johari−Goldstein process, and the fast process on the order of a picosecond are commonly observed in most glass-forming materials, suggesting that dynamics near the glass transition show general features, irrespective of the types of materials. From the polymer physics viewpoint, however, it is important to understand which properties are unique to glass-forming polymers and which are common for all glass-forming materials. It is believed in polymer science that structural relaxation of the main-chain backbone begins near the glass transition temperature T_g, meaning that the polymer chains begin to change their conformations near T_g. One of the aims of the paper is to see whether we could extract motions concerning conformational transitions from general dynamics of glass-forming materials.

The arrangement of this paper is as follows. After this Introduction and the Experimental Section, we will in section 3 summarize the characteristic features of dynamics in bulk polymers in the energy region of 0.01−10 meV, where we observed a slow process on a time scale from several tens to several hundreds of picoseconds as well as a fast process on the order of a picosecond. In section 4, we plot the characteristic times of the fast and slow processes of polybutadiene in its relaxation time map to try to identify the fast process and the slow process in glass-forming materials. In the discussion, we will show that the slow process could be assigned to an elementary process (E-process) for the conformational transitions. Hence, the slow process is termed the E-process here. In section 5, we will briefly summarize the results of the recent computer simulations for bulk amorphous polymers. In section 6, we will analyze the data in terms of a jump diffusion model with damped vibrations,[6] which is consistent with the recent results of the simulations for bulk polymers, and discuss the possible mechanism of the conformational transition based on the results.

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* Corresponding author: Tel. +81-774-38-3141, Fax +81-774-38-3146, e-mail kanaya@scl.kyoto-u.ac.jp.

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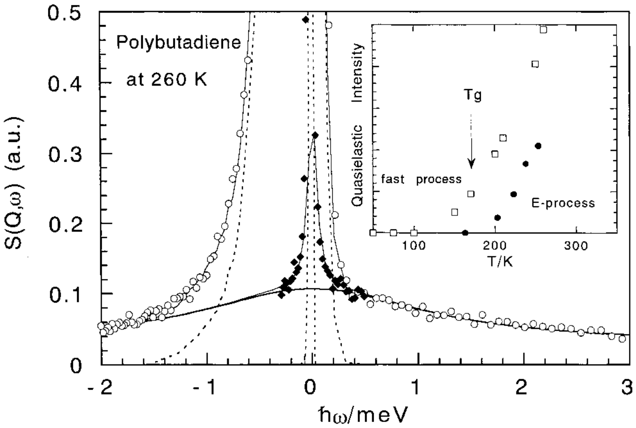

Figure 1. Dynamic scattering law $S(Q,\omega)$ of polybutadiene at 260 K measured with two neutron TOF spectrometers LAM-40 (○) and LAM-80 (◆). Dashed lines are the resolution functions of LAM-40 and LAM-80. Inset represents temperature dependence of integrated intensity of the fast process (□) and the E-process (●).

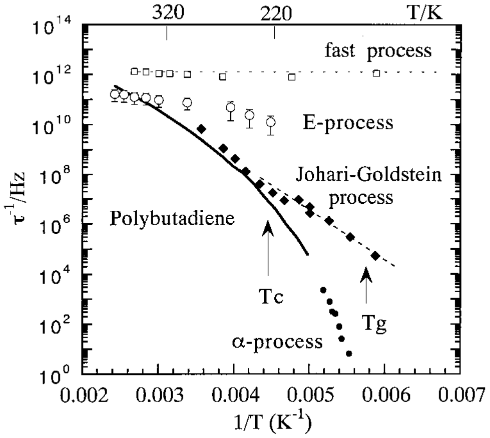

Figure 2. Relaxation time map of polybutadiene observed using various experimental methods (see text): QENS (LAM-40) (□), QENS (LAM-80) (○), NSE (◆), viscosity (−), ^{2}H NMR (●).

2. Experimental Section

Samples used for the experiments are *cis*-1,4-polybutadiene (PB) (molecular weight $M_w = 8.1 \times 10^5$; cis, trans, and vinyl contents = 95.7, 2.0, and 2.3%), *trans*-1,4-polychloroprene (PCP) ($M_w = 4 \times 10^5$; cis, trans, and vinyl contents = 6, 92, and 2%), polyisobutylene (PIB) ($M_w = 10^5$; Opanol B-100), and low-density polyethylene (PE) ($M_w = 8.06 \times 10^4$; Sumikathene G806, Sumitomo Chemical Industrial Co., Ltd.). The glass transition temperatures T_g's are 170, 200, and 228 K for PB, PIB, and PCP, respectively.

Quasielastic neutron scattering measurements were carried out with two inverted geometry time-of-flight (TOF) spectrometers LAM-40[17] and LAM-80[17,18] which are installed at a pulsed cold neutron source in KEK, Tsukuba. The LAM-40 and LAM-80 spectrometers have about 0.2 and 0.016 meV in energy resolution, 0−10 and 0−0.5 meV in energy window, and 0.2−2.6 and 0.2−1.73 Å^{-1} in magnitude of scattering vector, respectively. The data analysis method has been reported elsewhere.[6,19−21]

In quasielastic neutron scattering measurements we observe the dynamic scattering law $S(Q,\omega)$. In this experiment the observed $S(Q,\omega)$ is dominated by incoherent scattering from hydrogens because the incoherent atomic scattering cross section of hydrogen is much larger than the coherent and incoherent atomic scattering cross sections of other atoms as well as the coherent cross section of hydrogen.[22] The incoherent dynamic scattering law $S_{inc}(Q,\omega)$ is given by the Fourier transform of the self-part of the van Hove time−space correlation function $G_s(\mathbf{r},t)$,[23] which gives the probability of finding the same particle at a time $t = t$ and a position $\mathbf{r} = \mathbf{r}$ if there is a particle at a time $t = 0$ and a position $\mathbf{r} = 0$ in equilibrium.

The measurements were mainly performed far above T_g while the measurements of PB were extended to lower temperatures down to 223 K near T_g. Since polyethylene is a highly crystalline polymer, it is expected that the crystalline region affects local dynamics in the amorphous region. Therefore, measurements were performed on PE at temperatures only above the melting temperature T_m (=409 K).

3. Relaxation Processes in the Energy Range 0.01−10 meV

First of all, we consider relaxation processes in PB observed in the energy range from 0.01 to 10 meV, which corresponds to the time range of ~4 × 10^{-13} to ~4 × 10^{-10} s. Quasielastic neutron scattering spectra of PB at 260 K are shown in Figure 1 where both LAM-40 and LAM-80 spectra are combined. It is noted that the resolution functions of the spectrometers are not symmetric so that the LAM-80 data are not connected to the LAM-40 data on the left-hand side. In the energy region of 1−2 meV, the data show a sharp central component with a broad underlying component corresponding to a fast process having a picosecond time scale. This component appears at about 50 K below the glass transition temperature T_g which corresponds to the so-called Vogel−Fulcher temperature T_0, suggesting that the fast process is a precursor of the glass transition.[19,20,24] To demonstrate it, the quasielastic scattering intensity due to the fast process is plotted against temperature in the inset of Figure 1. The quasielastic spectra of the fast process can be well described by a Lorentzian function as indicated by a solid line in Figure 1. The half-width at half-maximum (hwhm) Γ of the Lorentzian function, corresponding to the inverse of the characteristic time, is almost independent of temperature. This means that the fast process is a kind of cage motion, but not an escape motion from the cage. It is noted that similar fast processes of picosecond order are observed in most amorphous materials including polymers[19−21,24−26] and low molecular weight glass-forming materials.[27,28] In addition to the fast process, a slow process (E-process) is detectable by the LAM-80 spectrometer in the energy region from 0.01 to 0.2 meV where the fast process is essentially a flat background. This slow process (E-process), which manifests itself as a broadening of the central sharp line in Figure 1, sets in at around the glass transition temperature T_g as shown in the inset of Figure 1. The quasielastic scattering spectra obtained on LAM-80 is also well described by a Lorentzian function (see Figure 4a), and the hwhm of the spectra depends on temperature, suggesting that the slow process (E-process) is a thermally activated process.

4. Relaxation Time Map of Polybutadiene

To identify the fast process and the E-process of PB, we have plotted the characteristic times τ of the two processes determined by QENS in a relaxation time map (Figure 2), where 1/τ determined using many other experimental techniques are also plotted versus inverse temperature. This map was first reported by Rössler et al.[29] to summarize the characteristic features of the dynamics of glass-forming materials. All the data reported in Figure 2 refer to *cis−trans*-polybutadiene with the molecular weight $M_w = 93\,000$ and the microstructure, cis:trans:vinyl = 47:46:7 except for the viscos-

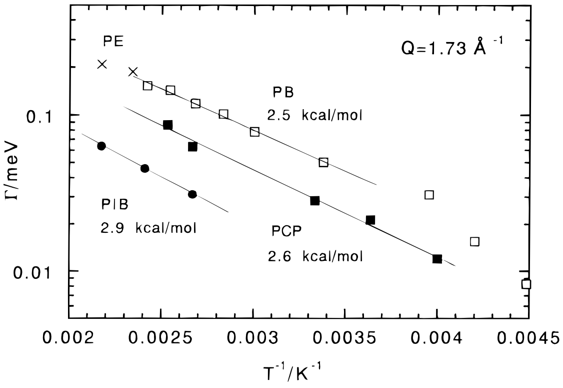

Figure 3. Temperature dependence of the half-width at half-maximum (hwhm) Γ of the Lorentzian function fitted to the E-process at $Q = 1.73$ Å^{-1}. Numerical values in the figure are apparent activation energies from the straight lines. (□) PB, (●) PIB, (■) PCP, (×) PE.

ity measurements, which were also performed on *cis*–*trans*-polybutadiene but for which the details of the microstructure were unclear. The present experiment was done on *cis*-1,4-polybutadiene ($M_w = 810\,000$, cis:trans:vinyl = 95.7:2.0:2.3) so that strict comparison is difficult among these polybutadienes. However, judging from the WLF parameters,[30] the difference of the relaxation times of the α-process among these PBs may be within 1 order of magnitude in the temperature range examined.

First we briefly explain each process observed in a glass-forming polymer. In the map the relaxation times measured by the neutron spin echo (NSE) technique[31,32] (solid diamonds) are displayed and compared with those of the α-process evaluated from viscosity data[33] (solid line). The relaxation times obtained by the NSE technique agree with those from the viscosity measurements above ~220 K, which is very close to the critical temperature T_c predicted by the mode coupling theory.[31,34] However, below ~220 K, the NSE data are decoupled from the α-process and show an Arrhenius behavior, which is a typical feature of the Johari–Goldstein (JG) process.[35,36] For polymers the JG process is often referred to as the β-process and sometimes identified with a side-chain motion or a motion due to internal degrees of freedom. However, it should be noticed that the JG process is observed not only in polymers but also in small molecular weight glass-forming materials,[29] and therefore, it can be considered as a universal feature of glass-forming materials, although the microscopic origin of the process is still unclear. The relaxation times evaluated using the stimulated echo technique with ^{2}H NMR[37] (solid circles in Figure 2) are smoothly connected to the viscosity data, showing that the technique probes the α-process.

The relaxation times of the fast process (open squares), which were obtained from the hwhm of the quasielastic scattering spectra by LAM-40, are also shown in the map. They are in the range 0.6–0.7 ps independent of temperature. These relaxation times are slightly different from those values previously reported (~0.3 ps).[31] This may be due to differences in method of analysis employed because the experimental spectra are almost identical.[38] As mentioned in section 3, similar fast processes are observed not only in polymers but also in low molecular weight glass-forming materials.

It is now considered that the three processes—the α-process, the Johari–Goldstein process, and the fast process—are commonly observed in most glass-forming materials including polymers and small molecules. In fact, the relaxation time map of a typical low molecular weight glass-forming material, *o*-terphenyl (OPT),[29] is very similar to that of PB. Therefore, these three processes should not be considered as special features of polymers but as common features of glass-forming materials. We will not discuss the details of these processes further since the aim of the present paper is to discuss an unfamiliar slow process (the E-process) which we consider to be related to the conformational transitions.

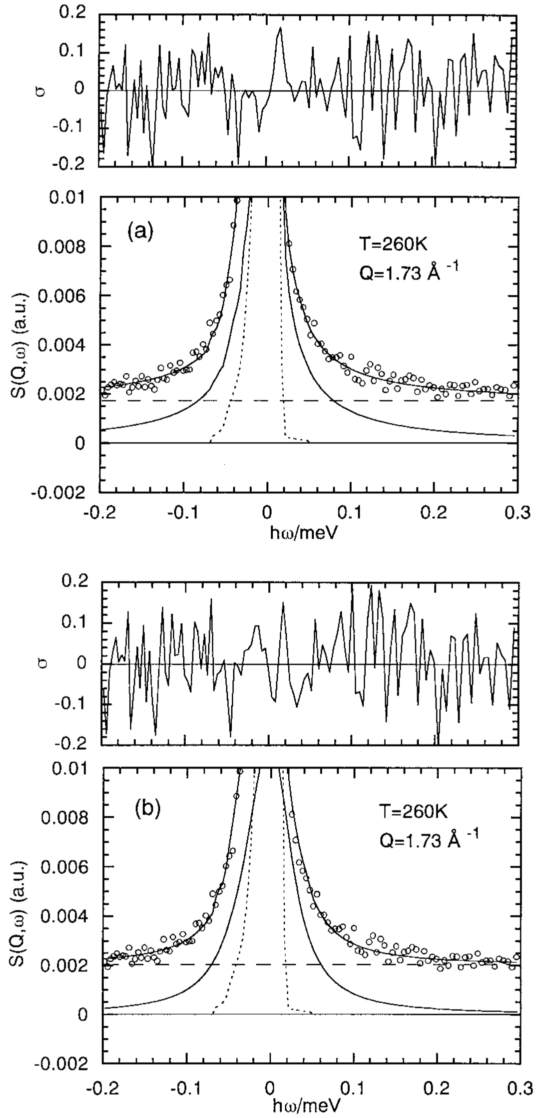

Figure 4. (a) Result of fit to LAM-80 spectrum of PB at 260 K by sum of dynamic scattering law $S_{HN}(Q,\omega)$ derived from the Havriliak–Negami function (eqs 1 and 2) (—), δ-function (···), and flat component (- - -). $1/\tau_{HN}$, α, and γ estimated in the fit are 0.033 meV, 0.66, and 0.90, respectively. (b) Result of fit to LAM-80 spectrum of PB at 260 K by sum of a single-exponential function (—), delta-function (···), and flat component (- - -). $1/\tau$ estimated in the fit is 0.027 meV.

The relaxation times (inverse of hwhm) of the E-process observed at $Q = 1.73$ Å^{-1} (open circles) are plotted in Figure 2. This process, which has not been reported for OTP, has relaxation times that are intermediate between the fast process and the α-process. In the high-temperature region above ~320 K the relaxation times for this process are almost the same as those of the α-process. It would appear from Figure 2 that the relaxation times of the E-process become longer than those of the α-process above ~400 K. This may be due to the experimental error or differences in the microstructure of the PB samples used in the experiments because the relaxation time of the local process (E-process) should always be shorter than or at least the same as that of the global process (α-process). The relaxation time of the E-process departs from the α-process below ~320 K; the temperature dependence is not as pronounced as for the α-process evaluated from the viscosity measurements. This weak temperature dependence suggests that the E-process has a lower activation energy, and it is associated with a local motion. The activation energy of the E-process evaluated above ~300 K is 2.5 kcal/mol (see also Figure 3), which corresponds to the barrier height of a single C−C bond rotation. It should be emphasized that this value is close to the activation energy predicted for conformational transitions in a polymer chain by computer simulations.[10] Furthermore, the observed relaxation times are of the same order as those predicted by the simulations, and the spatial scale probed by Q in this experiment is of the order of that expected for conformational transitions. These features strongly suggest that the E-process may be related to local conformational transitions.

Similar E-processes are observed in PIB, PCP, and PE. The hwhm's of the quasielastic scattering spectra of the E-process observed at $Q = 1.73$ Å^{-1} are plotted in the Arrhenius form for PB, PIB, PCP, and PE in Figure 3. The activation energies evaluated from the straight lines in the figure are 2.5, 2.6, and 2.9 kcal/mol for PB, PCP, and PIB, respectively. The value for PE was not evaluated because there are only two data points. The activation energies in the high-temperature region correspond approximately to the energy barrier for a single C−C bond rotation, suggesting that the E-process is an elementary process related to the conformational transitions.

Before going to the analysis, one must consider a possibility that the E-process is a part of the α-process, which is described by a stretched exponential function [$\exp(-(t/\tau)^{\beta})$; $0 < \beta < 1$], arising from a wide distribution of the relaxation time. To check this possibility, we fitted a dynamic scattering law, $S_{\mathrm{HN}}(Q,\omega)$, derived from the Havriliak−Negami (HN) function (see eqs 1 and 2) to the observed LAM-80 spectra. The HN function $\Phi^*(\omega)$ and $S_{\mathrm{HN}}(Q,\omega)$ are given by

$$\Phi^*(\omega) = \frac{1}{[1 + (i\omega\rho_{\mathrm{HN}})^{\alpha}]^{\gamma}} \tag{1}$$

$$S_{\mathrm{HN}}(Q,\omega) \propto -\frac{1}{\omega}\mathrm{Im}[\Phi^*(\omega)] \tag{2}$$

where α and γ are two parameters in the range ($0 < \alpha$, $\gamma < 1$) and τ_{HN} is a characteristic time of the relaxation process. According to Alvarez et al.,[39,40] the dynamic scattering law $S_{\mathrm{HN}}(Q,\omega)$ is numerically identical to the Fourier transform of the stretched exponential function, and the exponent β in the stretched exponential function is close to the product of the α and γ parameters in the HN function, $\beta \approx \alpha\gamma$. An example of the HN fit is shown in Figure 4a. For comparison, the Lorentzian fit is also displayed in Figure 4b. In these fits, the contribution of the fast process is described by a flat ω-independent component (dashed line) which is an adjustable parameter, and a δ-function (dotted line) is included to represent slow motions within the resolution function of the spectrometer. These contributions were convoluted with the resolution function of the spectrometer before fitting. Note that the quality of the HN fit without the δ-function is not as good as that with the δ-function although it is not shown here. As seen in Figure 4a,b, the qualities of the fits using either a Lorentzian or a HN function are almost identical, implying that it would be impossible only from the fits to distinguish which function better describes the LAM-80 spectra. However, it should be noted that the amplitude of the flat component in the Lorentzian fit is very close to the amplitude of the fast process estimated from the LAM-40 measurements while that in the HN fit is less than the observed one. Therefore, we have employed the Lorentzian fit in the present analysis to keep consistency between data collected on different instruments, although the Lorentzian fit gives a very simple picture (one time scale) in contrast to current analyses based on a stretched exponential function (distribution of characteristic time).[31,32,41,42] If the E-process is a high-frequency tail of the α-process, the present analysis corresponds to an assumption that the high-frequency tail is governed by the local conformational transitions in the present Q region.

5. Conformational Transitions

Before turning to the results, we briefly survey the results of computer simulations on conformational transitions in polymer chains. Pioneering work on an isolated polyethylene-like model was carried out by Helfand and co-workers[4,5] using the Langevin equation to show that single-bond rotations are possible in a polymer chain. Cooperative rotations are mainly manifested in counterrotations of two second-neighboring bonds separated by a trans bond. The key to understanding conformational transitions is that distortions in a polymer chain due to the strain brought about by the single-bond rotation can be relaxed through deformations of degrees of freedom in the neighborhood of a conformation-transforming bond. It was also shown by these simulations that the relaxation times of the elementary processes for the conformational transitions are in the range of several tens to several hundreds of picoseconds. The values of the relaxation times are of the same order of magnitude as the E-process probed by the present quasielastic neutron scattering measurements.

Following the work of Helfand and co-workers, molecular dynamics (MD) simulations on bulk amorphous polymers have recently been performed by several groups: on polyethylene-like models by Takeuchi and Roe[7,8] and by Boyd and co-workers,[9] on *cis*- and *trans*-polybutadienes by Gee and Boyd[10] and by Kim and Mattice,[11] and on polyisoprene by Moe and Ediger.[12,13] It was found that the motions of a polymer chain in the long time range are affected by the surrounding molecules which are acting as walls, while in the short time range the motions are surprisingly similar to those observed in an isolated chain by Helfand and co-workers, i.e., single-bond rotations as well as counterrotations of two second-neighboring bonds. Such conformational transitions are localized by deformations of other degrees of freedom of neighboring bonds, and the localization can be extended up to four or five bonds. In other words, because of their many degrees of freedom,

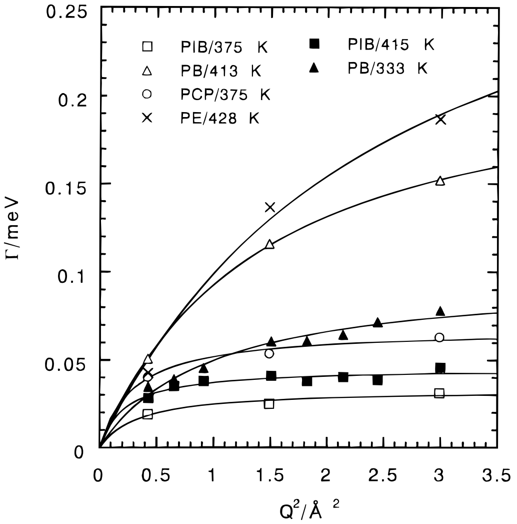

Figure 5. Q^2 dependence of the half-width at half-maximum (hwhm) Γ of the Lorentzian function fitted to the E-process: (□) PIB at 375 K, (■) PIB at 415 K, (△) PB at 413 K, (△) PB at 333 K, (○) PCP at 375 K, (×) PE at 428 K.

Table 1. Parameters of the Jump Diffusion Model for the Local Conformational Transitions

polymer	T/K	$\langle u^2\rangle$/Å^2	$\langle l^2\rangle$/A^2	τ_0/ps	D/Å^2 ps^{-1} [a]
PCP	300	0.092	21.2	161	0.022
PCP	375	0.21	19.9	61.1	0.054
PCP	395	0.25	17.5	43.6	0.067
PIB	375	0.14	18.3	144	0.023
PIB	415	0.19	28.3	91.6	0.052
PIB	460	0.23	25.1	54.2	0.077
PE	428	1.81	2.97	12.2	0.043
PE	460	2.09	2.38	10.8	0.034
PB[b]	296	0.44	14.5	81.3	0.032
PB[b]	318	0.49			
PB[b]	333	0.51	6.02	41.8	0.024
PB[b]	353	0.55	5.27	30.3	0.029
PB[b]	373	0.58	3.91	24.3	0.028
PB[b]	393	0.62	2.87	19.1	0.028
PB[b]	413	0.66	3.72	16.3	0.038

[a] Calculated from $D = \langle l^2\rangle/6\tau_0$. [b] Data reported in ref 6.

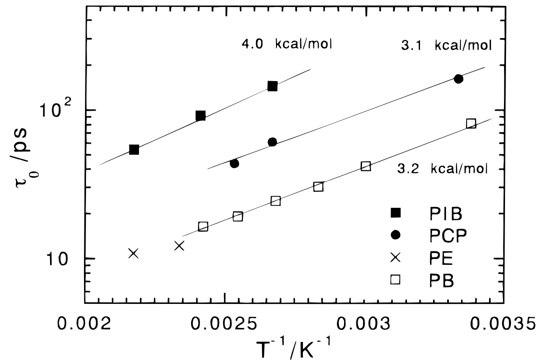

Figure 6. Temperature dependence of relaxation time for the conformational transitions evaluated using the jump diffusion model with damped vibrations: (□) PB, (●) PIB, (■) PCP, (×) PE.

polymer chains are sufficiently flexible to make a conformational transition localized. Furthermore, it was found that even in bulk, the apparent activation energy of an elementary process for the conformational transitions is roughly the same as the energy barrier height of a single C−C bond rotation. This is again the same result as for an isolated chain.

To analyze the quasielastic neutron scattering (QENS) data for the E-process, we require an analytical model. There are many models for conformational transitions such as the Hall−Helfand model, the generalized diffusion and loss (GDL) model, and many other models.[1] These models have been used to describe the orientational relaxation in a polymer chain. The QENS data provide additional information on the spatial scale of the molecular motions; since none of the models quoted above take into account the spatial scale of the motions, they cannot be used to interpret the QENS data. To extract the spatial information, we require a model describing the Q dependence explicitly. Hence, we analyze the temperature and Q dependence of the E-process using the simplified jump diffusion model presented previously.[6] This model incorporates in a simple fashion diffusional (conformational) jumps separated by a waiting time τ_0 during which damped vibrational motions take place. It is noted that the physics of actual conformational transitions seen in recent MD simulations are approximately consistent with this simple picture.

6. Results and Discussion

In the analysis we focus on the Q dependence of hwhm of the E-process. The observed hwhm Γ of the Lorentzian function of the E-process is plotted against Q^2 for PIB, PCP, and PE in Figure 5 where the reported PB data[6] are also included for comparison. The theoretical equation of the jump diffusion model (see eq 5 in ref 6) was fitted to the observed Q dependence, and the results of the fits are given by solid lines in Figure 5. The agreement is very good, suggesting that the model can describe the E-process. From the fit, we extracted the root-mean-square jump distance $\langle l^2\rangle^{1/2}$ and the relaxation time of the elementary process for the conformational transitions or the average rest time in a conformation, τ_0. The results are summarized in Table 1, including the reported PB data[6] for comparison. The relaxation time is plotted versus $1/T$ in Figure 6. The temperature dependence of the relaxation time is well represented by the Arrhenius equation in the temperature range examined, and the activation energies evaluated are 4.0, 3.2, and 3.1 kcal/mol for PIB, PCP, and PB, respectively. These values are close to the barrier heights for a single C−C bond rotation, corresponding to the prediction of the MD simulations. The activation energy for PIB is slightly higher than the energy barrier of the C−C bond rotation. This may be due to the two methyl groups hindering rotations of the C−C bond in the backbone.

The root-mean-square jump distance $\langle l^2\rangle^{1/2}$ for the conformational transition is plotted against T in Figure 7 for PB, PE, PCP, and PIB. The jump distance is independent of temperature for each polymer within experimental error except the value for PB at 296 K, suggesting that the mechanism of the conformational transitions does not change in the temperature range examined. The increase of $\langle l^2\rangle^{1/2}$ of PB at 296 K may be because cooperativity of motions becomes larger with decreasing temperature.

For PB and PE which have no side groups, the root-mean-square jump distance $\langle l^2\rangle^{1/2}$ is around 2 Å. In a previous paper,[6] assuming that the conformational transitions of PB are localized within three bonds, we estimated the value of $\langle l^2\rangle^{1/2}$ to be 2.06 Å. This agrees very well with the observed value. Under the same assumption, we calculated the value of $\langle l^2\rangle^{1/2}$ for PE. The calculated value is 1.8 Å, which is also very close to the

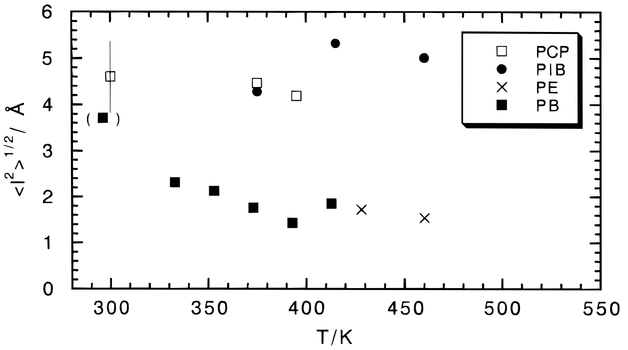

Figure 7. Root-mean-square jump distance $\langle l^2\rangle^{1/2}$ for the conformational transitions evaluated using the jump diffusion model with damped vibrations: (■) PB, (●) PIB, (□) PCP, (×) PE.

observed value. It is therefore concluded that the conformational transitions of PB and PE are localized within three bonds, at least, on average. On the other hand, the $\langle l^2\rangle^{1/2}$ for PIB and PCP are around 5 Å, being rather large compared with those of PE and PB, suggesting that the conformational transitions of PIB and PCP are not localized within three bonds. In other words, the distortions due to the conformational transitions are extended to more than three bonds. Exact estimates are impossible because of the many degrees of freedom. This delocalization of the conformational transitions in PIB is surely related to the presence of the side groups. The PIB chains are relatively rigid compared with PE and PB chains because two methyl groups hinder the rotation of main-chain carbons, so that the strain due to the conformational transition cannot be relaxed within the neighboring three bonds. The delocalization in PCP may be due to the trans effect and/or the large chlorine atoms.

Very recently, Moe and Ediger[43] have calculated the coherent intermediate scattering function $S_{\mathrm{coh}}(Q,t)$ on the basis of MD simulations for bulk polyisoprene and compared the results with the NSE data.[41] It was shown that the full $S_{\mathrm{coh}}(Q,t)$ can be approximated by considering only the self-terms and the cross-terms localized to within a few repeat units along the chain. This supports the picture on localization of conformational transitions presented here although their data treatment is different from ours.

7. Conclusions

In this work, we reported quasielastic neutron scattering experiments on polyisobutylene (PIB), *trans*-1,4-polychloroprene (PCP), and polyethylene (PE) in the energy range 0.01−10 meV. Similar to the results of *cis*-1,4-polybutadiene (PB) reported earlier,[6] the fast process on the picosecond time scale and the E-process having a time scale from several tens to several hundreds of picoseconds were observed in these polymers far above the glass transition temperature T_g. It was demonstrated that the fast process is commonly observed in glass-forming polymers while the E-process is characteristic only to polymers performing conformational transitions through torsional motions. The spectra of the E-process were fitted with a Lorentzian function to evaluate the characteristic time as a function of T and Q. This single Lorentzian fit gives a simple picture (one time scale) in contrast to current analyses based on a stretched exponential function (distribution of characteristic time). The activation energy of the E-process and the magnitude of the characteristic time implied that the E-process is an elementary process for the conformational transitions. Hence, the Q dependence of the characteristic time was analyzed in terms of a jump diffusion model with damped vibrations which is consistent with the results of the recent molecular dynamics (MD) simulations on the conformational transitions of bulk amorphous polymers. It was suggested that conformational transitions in PB and PE are localized within three bonds while those in PIB and PCP extend to more than three bonds. The delocalization in PIB was assigned to the chain rigidity due to two side methyl groups.

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