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Molecular motion of isolated polybutadiene chains tethered on the fresh surface of polytetrafluoroethylene

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The polybutadiene (PBD) chains tethered on the fresh surface of a polytetrafluoroethylene (PTFE) were produced by a block copolymerization of PTFE with 1,3-butadiene in vacuum at 77 K. The extremely low segmental density of the tethered chains was estimated by a spin labelling technique. The tethered chains can be regarded as 'isolated polymer chains'. The PBD tethered chain has an unpaired electron at the chain end. We studied the molecular mobility of the PBD tethered chains by electron spin resonance (e.s.r.) spectroscopy, using the PBD chain end radical as a probe. The site exchange motion between two conformations at the chain end was observed in the temperature range 77–173 K and the rate of the exchange motion was determined by spectral simulations. The tethered chains are mobile even below 218 K which is a glass transition temperature of 1,4-PBD in the bulk. The high mobility of the PBD chains tethered on the PTFE surface is attributed to: the PBD chains have a very large space around the chains because of an extremely low segmental density on the PTFE surface. © 1997 Elsevier Science Ltd.

(Keywords: polybutadiene; isolated chain; polytetrafluoroethylene surface)

INTRODUCTION

Numerous studies on molecular motion of polymer chains in solid state or in solution have been reported. In these systems, a molecular mobility of polymer chains strongly depends on surroundings. The mobility of the chains in solid state depends on the free volume related to the interaction between the inter-polymer chains, or the intra-polymer chains. The segmental density in the vicinity of the surface is lower than that in the bulk. The low segmental density results in a lower glass transition temperature in the vicinity of polymer surface than that in the bulk[1,2]. In dilute solution, the mobility is affected by the interaction between the polymer chains and solvent molecules. Thus, the mobility is a function of inter-molecular and intra-molecular interactions. It is important to evaluate individually the interaction and understand a fundamental physical property of the individual polymer chain.

In low molecular weight compounds, the mobility of isolated molecules has been reported, in which the low molecules are trapped in argon matrix[3]. The mobility is high even at extremely low 4 K due to an isolated molecule because of the very weak interaction with the matrix. In general, an isolated polymer chain in a frozen argon matrix cannot be obtained because a polymer is not gaseous at any temperature.

Iwasaki *et al.* observed the e.s.r. spectra of the PBD chain end radical in a urea canal complex[4]. In the canal complex, each PBD chain is isolated from neighbouring polymer chains by the host matrix. However, a conformation of the PBD chains is restricted by the canal wall. Thus the mobility in the canal would reflect a specific conformation as *trans*-PBD[5].

If polymer chains have a large space around the chains and their aggregation is inhibited, the chains should be scarcely affected by other chains and can be regarded as 'isolated polymer chains' in vacuum.

In our previous papers: the alkyl radical, $-CH_2CH_2\cdot$, of polyethylene (PE) tethered on a PTFE surface has high mobility even at 77 K[6–8]. The peroxy radicals at the end of PE chains tethered on the PTFE surface has also high mobility[9]. This high mobility was interpreted in terms of: (1) the PE molecules were present in an extremely low segmental density on the PTFE surface in vacuum; and (2) the PE chains are prevented from their aggregation because one end of the chain is tethered on the PTFE surface and PE is immiscible with PTFE. Thus, the PE chains can be regarded as 'isolated PE chains'. However, the degree of contact of the tethered PE chains with the neighbour chains remains pending as the chain length of the tethered PE chains still cannot be characterized.

In this paper, we produced the PBD chains tethered on the PTFE surface in order to observe an intrinsic molecular motion of the individual PBD chains. The molecular weight of the tethered PBD chains was characterized and the mobility of chain end radicals of

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PBD was studied by e.s.r. spectroscopy using the PBD chain end radical as a probe. We will discuss the molecular mobility of the PBD chains regarded as 'isolated polymer chains'.

EXPERIMENTAL

PTFE powder (Fluon G163, Asahi Glass Co., Ltd.) was used without further purification. 1,3-Butadiene monomer (Tokyo Chemical) was purified by a freeze–pump–thaw method.

The PBD chains tethered on the fresh surface of PTFE were produced as follows: The PTFE powder (1.50 g) was fractured with 1,3-butadiene monomer (7.5×10^{-5} mol) at 77 K in vacuum by a home-made vibration glass ball mill[10]. The ball-milling of PTFE powder produces PTFE mechano radicals[10] which are chain-end type radicals and trapped on the fresh surface[11] of PTFE. The PTFE mechano radicals can initiate the radical polymerization[12] of 1,3-butadiene monomer at 77 K in vacuum when the PTFE radicals come into contact with the monomer by physical mixing during the milling. The radical polymerization of 1,3-butadiene monomer proceeds and then the PBD chains tethered on the PTFE surface are produced. The PBD chains have an unpaired electron at the propagating end.

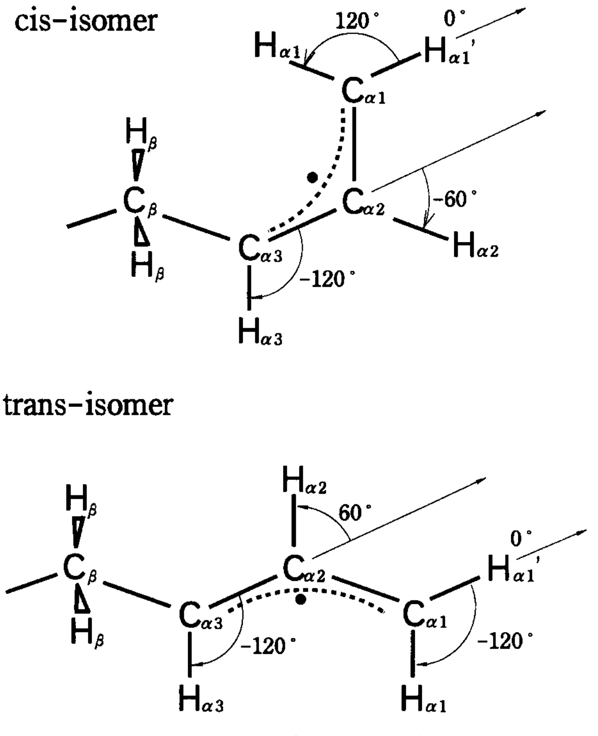

Figure 1 *Cis*- and *trans*-isomer of the allyl radical at the PBD chain end

After polymerization, the e.s.r. sample tube connected to the glass ball mill was placed into liquid nitrogen, and the sample was dropped into the e.s.r. sample tube within 1 s by turning it upside down. A residual monomer was still present in this sample since the monomer did not react perfectly. This wet sample is called the W-sample. Another sample was prepared. After the milling, a residual monomer was evacuated at 183 K for 1 h under a pressure below 10^{-4} torr. This dry sample is called the D-sample.

E.s.r. spectra were observed at a low microwave power level to avoid power saturation and with 100 kHz field modulation using JEOL JES-FE3XG and JEOL JES-RE1XG spectrometers (X-band) coupled to NEC PC-9801 microcomputers. The signal of 1,1-diphenyl-2-picrylhydrazyl (DPPH) was used as a *g*-value standard. The magnetic field was calibrated with well-known splitting constants of Mn^{2+} in MgO.

SPECTRAL SIMULATION

Hori *et al.* have reported[13] a computer program based on a conformation exchange due to a ring inversion of cyclohexyl radicals in which the radicals have one α proton (H_α). This program employs the line shape equation derived by Heinzer[14] based on a density matrix theory in the Liouville representation. Heinzer's equation is identical with that derived from the modified Bloch equation. Sakaguchi *et al.* have modified[7] the program developed by Hori *et al.* to simulate an e.s.r. spectrum of an alkyl radical.

We used the program modified[7] by Sakaguchi *et al.* to simulate an e.s.r. spectrum of a propagating allyl radical of PBD chain end as shown in *Figure 1*, which has four H_αs with an anisotropic hyperfine splitting (hfs) (A_x, A_y, and A_z) and two β protons (H_β) with an isotropic hfs (A_β). The intramolecular coordinates based on the principal axes of the hfs tensor of H_α are assumed: A_x axis is parallel to p_π occupied by the unpaired electron at the α carbon (C_α), A_z axis is along the direction to the C_α–H_α bond axis, and A_y axis is perpendicular to both the A_x and A_z axes. We assumed two isomers, *cis*- and *trans*-, for the chain end allyl type radicals (*Figure 1*). $C_{\alpha1}$–$H_{\alpha1}$, $C_{\alpha1}$–$H_{\alpha1}'$, $C_{\alpha2}$–$H_{\alpha2}$, and $C_{\alpha3}$–$H_{\alpha3}$ are put at the positions to $C_{\alpha3}$–$C_{\alpha2}$ bond axis with angles of 120°, 0°, −60°, and −120° in *cis*-isomer, respectively. In *trans*-isomer, $C_{\alpha1}$–$H_{\alpha1}$, $C_{\alpha1}$–$H_{\alpha1}'$, $C_{\alpha2}$–$H_{\alpha2}$, and $C_{\alpha3}$–$H_{\alpha3}$ are put at the positions to $C_{\alpha3}$–$C_{\alpha2}$ bond axis with angles of −120°, 0°, 60°, and −120°, respectively. *Figure 2* shows two conformations of the PBD chain end radicals which

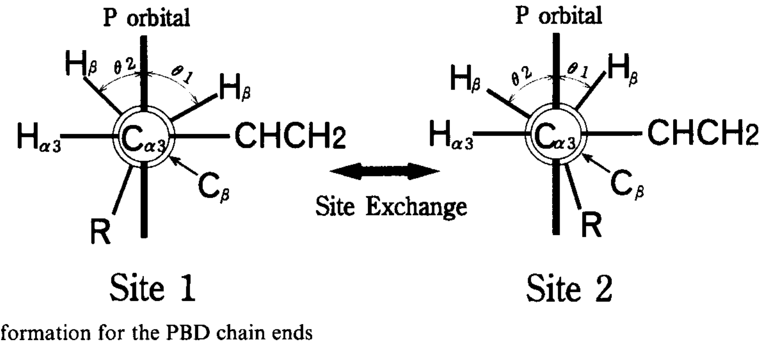

Figure 2 Two sites of the conformation for the PBD chain ends

have sites 1 and 2. θ_1 and θ_2 are dihedral angles of the $C_{\alpha3}$–H_β bond axis relative to the p_π axis.

RESULTS AND DISCUSSION

Characterization of tethered PBD chain

In an extremely low PBD fraction in the sample, it was difficult to estimate the PBD fraction by a pyrolysis. Accordingly, we developed the spin labelling technique to determination of the PBD fraction 100 × PBD(g)/[PBD(g) + PTFE(g)] (%) of the sample. Rockenbauer *et al.* reported[15] that 2,6-dichloronitrosobenzene (DCNB) forms a nitroxide radical in the reaction with macromolecule chains containing C=C double bonds. In our previous paper[16], the spin labelling technique was used to determine the extremely low PBD fraction tethered on PTFE surface. The absolute amount of the nitroxide radicals produced after the reaction is stoichiometrically related to that of the double bond.

We obtained a calibration curve[16] to estimate an amount of the PBD chains tethered on the PTFE surface as follows: Some toluene solutions of PBD in the concentration of 0.199–13.5 ($\mathrm{g\,l^{-1}}$) containing a small amount of DCNB were prepared. As the reaction in e.s.r. sample tube is proceeding at room temperature, the e.s.r. spectral intensity of nitroxide radicals increases and have a maximum. A calibration curve for the determination of the absolute amount of PBD chains was obtained by plotting the maximum value of the spectral intensity against the concentration of the solution.

The powder sample (0.10 g) of the PBD chains tethered on the PTFE, in which the PBD propagating radicals disappeared, was dilute in toluene (1 ml) containing a small amount of DCNB. The e.s.r. spectrum of produced nitroxide radicals was observed at room temperature. The spectral intensity of the nitroxide radicals also increased and had a maximum with storage time. The amount of PBD chains tethered on the PTFE surface can be estimated from the maximum value of the intensity and the calibration curve.

The PBD fraction of the D-sample was estimated to be 2.5×10^{-2}%. The average degree of polymerization is calculated to be 41 using concentration of the tethered point (6.8×10^{16} $\mathrm{spins\,g^{-1}}$)[7].

$\{\langle R_0^2\rangle_f/N\}^{1/2}$ for a PBD was reported to be 4.02 for *cis*-PBD and 5.80 (Å) for *trans*-PBD[17], where $\langle R_0^2\rangle_f$ is mean square end-to-end distance for a model of freely rotating chain around a single bond and N is a degree of polymerization. Mean square radius, $\langle S_0^2\rangle_f$, of gyration is given by $\langle S_0^2\rangle_f = \langle R_0^2\rangle_f/6$. Therefore $2\langle S_0^2\rangle_f^{1/2}$ of the PBD tethered on the PTFE can be estimated approximately to be 21 Å or 30 Å for *cis*- or *trans*-PBD tethered chains, respectively.

The area per tethered point on the PTFE surface, $A = 3.1 \times 10^3$ $\mathrm{Å^2\,spin^{-1}}$, was deduced from the concentration of the tethered point and the specific surface area ($2.1\,\mathrm{m^2\,g^{-1}}$)[7]. $2\langle S_0^2\rangle_f^{1/2}/A^{1/2}$ is a good measure of the degree of contact of tethered chains with neighbour tethered chains, where $A^{1/2}$ is an average distance between one tethered point and the neighbour tethered points. The $2\langle S_0^2\rangle_f^{1/2}/A^{1/2}$ for the *cis*- and *trans*-PBD tethered chain was obtained to be 0.38 and 0.54. Since these values are smaller than 1.0, the tethered chains have no contact with each other. In other words, the PBD tethered chains can be regarded as 'isolated polymer chains'. It is confirmed that the PBD tethered chains in the W-sample having an extremely low PBD fraction of 3.0×10^{-2}% can also be regarded as 'isolated polymer chains', though the chains are surrounded by 1,3-butadiene monomer molecules.

Structure of the PBD chain end radical

The e.s.r. spectrum of PBD chain end radicals in the W-sample observed at 193 K is shown in *Figure 3A*. The chain end radicals are much stable at higher temperatures than the melting point of 1,3-butadiene monomer. The spectrum of 2 × 6 lines was assigned to the chain-end allyl type radicals, $C_\beta(H_{\beta2})_2{-}C_{\alpha3}H_{\alpha3}\,\dot{\cdots}\,C_{\alpha2}H_{\alpha2}\,\dot{\cdots}\,C_{\alpha1}\ (H_{\alpha1})_2\cdot$, which have large hfs constants (*ca.* 1.5 mT) due to $H_{\alpha1}$, $H'_{\alpha1}$, $H_{\alpha3}$, and two H_βs and small hfs constant (*ca.* 0.4 mT) due to $H_{\alpha2}$. A five line spectrum of PBD chain end radicals for the W-sample was observed at 77 K as shown in *Figure 3B* with solid line because the rotation around the $C_{\alpha3}$–C_β bond is hindered. This five line spectrum is similar to the spectrum of the PBD chain end radicals observed in urea canal complexes reported by Iwasaki *et al.*[4]. First, the simulated spectrum shown in *Figure 3B* with a broken line is calculated by assuming the conditions: (1) the PBD chain end radical takes only a *trans*-form; and (2) the PBD chain end radicals take two symmetrical conformations (two sites) (*Figure 2*) having equal population of each site and the site exchange motion is frozen. Hfs constant A_β due to β hydrogen is calculated by using the relation $A_\beta = 2Q_\beta\rho_c\cos^2\theta$[18], where Q_β is the empirical constant and ρ_c is the spin density on the α_3 carbon atom. θ_1, θ_2, and $Q_\beta\rho_c$ can be determined by way of trial and error. For instance, several theoretical spectra are calculated and compared with the experimental spectra. The broken line in *Figure 3B* shows the calculated spectrum by

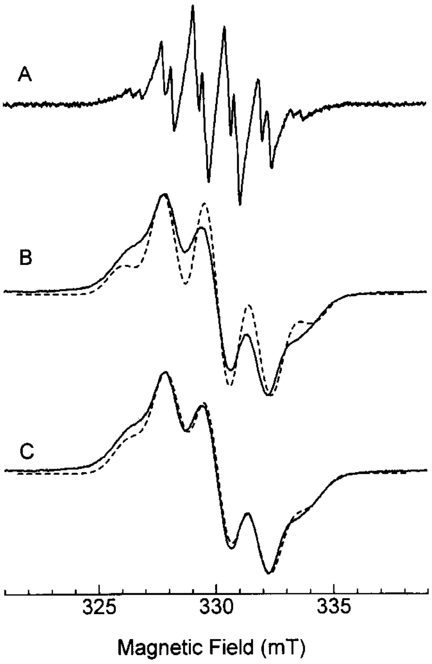

Figure 3 E.s.r. spectra of the PBD chain end radicals of the W-sample observed at 193 K (A) and at 77 K (B, C). The simulated spectrum (broken line in B) is obtained as follows: the PBD chain end radicals are *trans*-form, the spectrum is composed of two components spectra from sites 1 and 2 assuming equal population of each site, and the molecular motion of the PBD chains is frozen. The spectrum (broken line in C) is calculated as broken line in B except that the mole fraction of *cis*-isomer is 40%

assuming the anisotropic constants of $A_x = 1.43$, $A_y = 2.33$, and $A_z = 0.72\,\mathrm{mT}$[19] for $H_{\alpha 1}$, $H'_{\alpha 1}$, and $H_{\alpha 3}$, the small value hfs constant 0.42 mT for $H_{\alpha 2}$, and two isotropic hfs constant A_βs of 0.53 and 1.76 mT for two H_βs. The isotropic hfs constant $[A_{\mathrm{iso}} = (A_x + A_y + A_z)/3 = 1.49\ \mathrm{mT}]$ due to H_α is consistent with the hfs value due to H_α of allyl type radicals obtained by other workers[4,20]. Iwasaki *et al.*[4] estimated the value of $Q_\beta \rho_c$ to be 1.70 mT for allyl type radical from experimental values of Q_β and ρ_c obtained by Fessenden and Schuler[21] and determined the conformation of PBD chain end radical in the urea canal complex. The A_β values of 0.53 and 1.76 mT correspond to the dihedral angles, $\theta_1 = 66°$ and $\theta_2 = 42°$. The conformational structure of the radicals and the value of $Q_\beta \rho_c$, 1.59 mT, are almost the same as the results reported by Iwasaki *et al.*[4].

The calculated spectrum (broken line) in *Figure 3B* is similar to the reported spectrum[4] of the PBD chain end radicals in the urea canal complex in which the PBD chains keep a *trans* form[5]. However, the peak positions and the relative intensities of five lines for the calculated spectrum (broken line) are in disagreement with those for the observed spectrum (solid line) in *Figure 3B* of the allyl radicals. This disagreement suggests that both *cis*- and *trans*-isomers of PBD chain end radicals should be considered. A coexistence of these isomers is also reasonable because the PBD chains propagate in the free space and the form of the PBD chain end radicals is not restricted by other molecules such as a urea in the canal complex.

Next, the simulated spectrum is calculated by considering the contribution of the *cis*-isomer. The broken line in *Figure 3C* shows a simulated spectrum as that in *Figure 3B* except that the mole fraction of *cis*-isomer is 40%. The simulated spectrum is in good agreement with the observed spectrum (solid line).

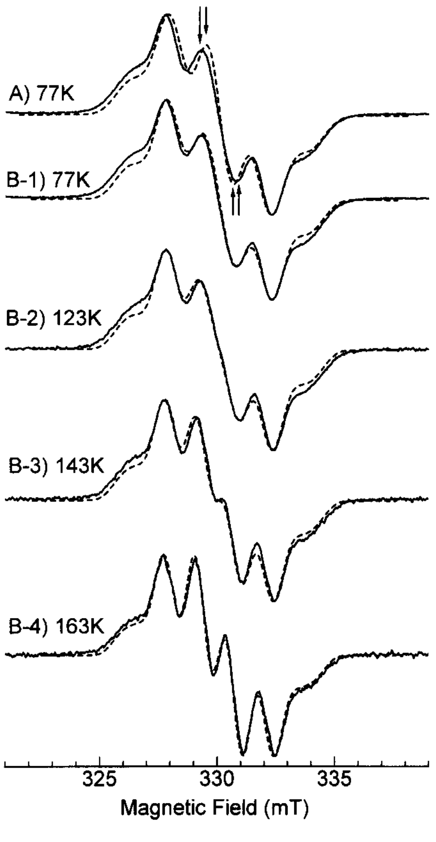

Figure 4 E.s.r. spectra of the PBD chain end radicals with solid line for the D-sample observed at 77, 123, 143, and 163 K. The simulated spectrum (broken line in A) is identical with a broken line in *Figure 3C*. The simulated spectra (broken lines in B) are calculated by assuming the site exchange rate of 30, 67, 120, and 200 MHz, respectively

Thus, it can be concluded that the tethered PBD chain end radicals have both *cis*- and *trans*-isomers.

Site exchange motion at the end of PBD chains tethered on the PTFE surface

The e.s.r. spectra observed at 77, 123, 143, and 163 K for D-sample are shown in *Figure 4* with solid lines. The solid line in A is identical with that in B-1. The simulated spectrum (broken line) in A is also the same as the broken line in *Figure 3C*. The simulated spectrum in A is a slightly poor fit to the observed spectrum because the peak positions marked with arrows in broken line spectrum still deviate from those in solid line (the positions and relative intensities of the lines for the observed spectrum are slightly different with those for the calculated spectrum). These deviations were not improved with various fractional amounts of *cis*-isomer. This suggests that another factor is required to improve the deviations. These results lead us to consider that the PBD chain end radicals in the D-sample may begin the exchange motion between sites 1 and 2, which is shown in *Figure 2*, even at 77 K. The mole fraction, 40%, of *cis*-isomer is fixed while the spectral simulation for molecular motion is carried out. The simulated spectrum (broken line) in *Figure 4B-1* is calculated as a broken line in A except that the rate of site exchange motion is 30 MHz. The simulated spectrum is in good agreement with the observed spectrum. Thus, it can be concluded that the PBD chain end radicals in the D-sample have the site exchange motion around the $C_{\alpha 3}$–C_β even at 77 K with a rate of 30 MHz.

The spectral change from 5- to 6-lines in *Figure 4* is induced with increasing temperature. The onset of spectral changes is clearly evident at 143 K. The spectral intensity does not decay below 183 K (*Figure 5*) and the spectral change is reversible in the temperature range 77–183 K. Thus, the spectral changes are attributed to a temperature dependence of a molecular motion.

The simulated spectra (broken lines) for the spectra observed at 123, 143, and 163 K are obtained as the

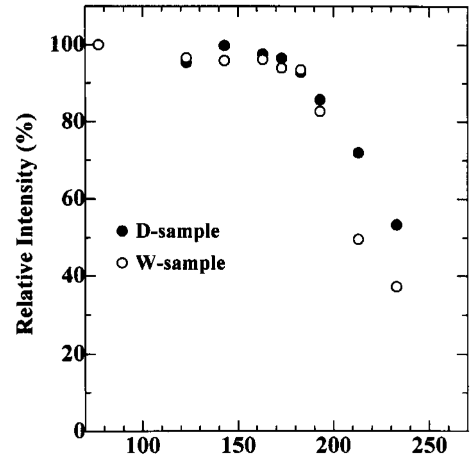

Figure 5 Decay curve of the PBD chain end radicals for the D-sample (solid circle) and for the W-sample (open circle)

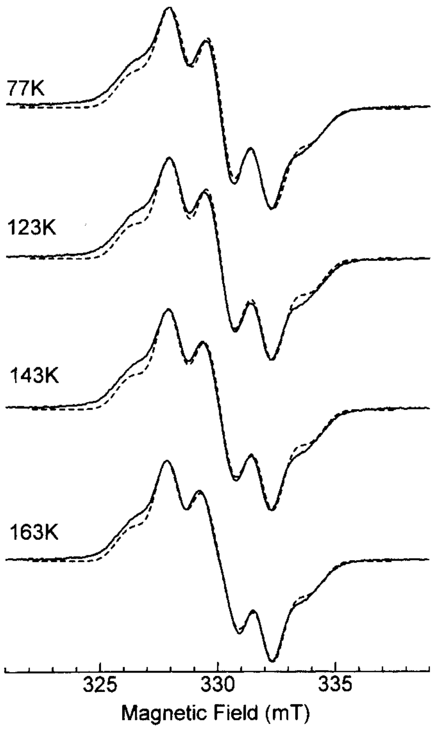

Figure 6 E.s.r. spectra of the PBD chain end radicals with solid line for the W-sample, which are observed at 77, 123, 143, and 163 K. The simulated spectra (broken lines) are calculated by assuming the site exchange rate of frozen, 22, 35, and 55 MHz, respectively

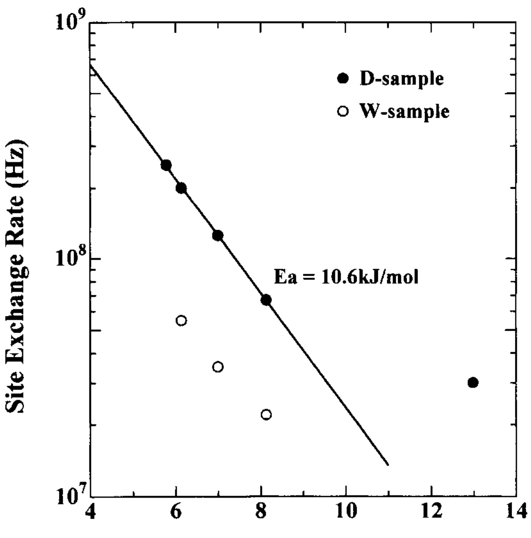

Figure 7 Arrhenius plot of the site exchange rate for the D-sample chain (solid circle) and for the W-sample (open circle)

broken line in *Figure 4B-1* except the site exchange rate of 67, 120, and 200 MHz, respectively. The simulated spectra are in good agreement with the observed spectra. The spectral change is interpreted in terms of site exchange motion of the chain end radicals. The PBD chains tethered on the PTFE surface are more mobile even below 218 K which is a glass transition temperature of 1,4-PBD in the bulk[22].

How does the presence of the residual monomer affect the molecular motion of the PBD chains? If the monomers in solid state are present around the PBD chains, the molecular density around the chains increases. The molecular motion of the PBD chains may be restricted by the 1,3-butadiene monomer. In order to elucidate the effect of the monomer on the molecular motion of the PBD chains, the PBD chain end radicals in the W-sample (see Experimental section), in which the residual monomer are present in the sample, were observed. *Figure 6* shows the e.s.r. spectra with solid line of the W-sample observed at 77 K, 123 K, 143 K, and 163 K which are below the melting point of 1,3-butadiene. The observed spectrum at 77 K is identical with the spectrum shown in *Figure 3B* with a solid line. The other spectra observed at higher temperatures are similar to the spectrum observed at 77 K. However, the spectra change still occurs slightly with increasing temperature. The simulated spectra are shown with broken lines in *Figure 6*. The simulated spectra observed at 123, 143, and 163 K are calculated as the broken line in *Figure 3B* except that the site exchange motions are 22, 36, and 55 MHz, respectively (the mole fraction of *cis*-isomer is 40%). The simulated spectra are in good agreement with the observed spectra. The site exchange rates of the W-sample are lower than that of the D-sample. The molecular motion of the PBD chains are found to be restricted by the solid residual monomer. The spectral intensity for the W-sample decayed much faster above 183 K than that for the D-sample, as shown in *Figure 5*. In addition, as shown in *Figure 3A*, the e.s.r. spectrum line shape is sharp above the melting point of 1,3-butadiene and the molecular motion is more rapid. That is, the PBD chain ends tethered on the PTFE surface was plasticized by the monomer above the melting point. These facts suggest that the residual monomer in the W-sample surely affects the molecular motion of the PBD chains.

The PBD chain in the D-sample can be regarded as an isolated chain as well as the isolated PE chains[6–8] on the PTFE surface. The isolated PBD chains are found to have a high mobility because of the low segmental density and the immiscibility between PBD and PTFE.

The site exchange rates determined by spectral simulations are plotted against the inverse temperature in *Figure 7*. The apparent activation energy of the site exchange motion for the D-sample is estimated to be 10.6 kJ mol^{-1}. Both the activation energy and the temperature range of the site exchange motion occurring are higher than those values reported[7] for the PE chain tethered on the PTFE surface. These facts suggest that the intrinsic flexibility of the individual PBD chains is different from that of PE chains, i.e. PBD chains are inherently stiff in comparison with PE chains because of the rotational restriction around a double bond in PBD chains.

CONCLUSIONS

The PBD chain ends tethered on the fresh surface of PTFE in vacuum were produced by a copolymerization with 1,3-butadiene.

The extremely low PBD fraction of the PBD chain tethered on the PTFE surface was quantitatively estimated by a spin-labelling method developed by us. The tethered PBD chains have no contact with each other and can be regarded as isolated chains.

The molecular motion of the PBD chain ends tethered on the PTFE surface in vacuum was observed by e.s.r.

spectroscopy. The isolated PBD chain ends have a site-exchange motion between two sites even at 77 K. The high mobility of tethered PBD chains is attributed to: (1) the tethered PBD chains have an extremely low segmental density on the PTFE surface in vacuum; and (2) the PBD chains are prevented from their aggregation because one end of the chain is tethered on the PTFE surface and PBD is immiscible with PTFE. The tethered PBD chains on the PTFE surface behave as isolated chains in vacuum and reveal the intrinsic mobility of the individual PBD chains.

REFERENCES

1. Mayes, A. M., *Macromolecules*, 1994, **27**, 3114.
2. Kajiyama, T., Tanaka, K. and Takahara, A., *Macromolecules*, 1995, **28**, 3482.
3. Adrian, F. J., Cochran, E. L. and Bowers, V. A., *J. Chem. Phys.*, 1973, **59**, 3946.
4. Ohmori, T., Ichikawa, T. and Iwasaki, M., *Bull. Chem. Soc. Jpn.*, 1973, **46**, 1383.
5. White, D. M., *J. Am. Chem. Soc.*, 1960, **82**, 5678.
6. Sakaguchi, M., Yamagichi, T., Shimada, S. and Hori, Y., *Macromolecules*, 1993, **26**, 2612.
7. Sakaguchi, M., Shimada, S., Hori, Y., Suzuki, A., Kawaizumi, F., Sakai, M. and Bandow, S., *Macromolecules*, 1995, **28**, 8450.
8. Sakaguchi, M., Shimada, S., Yamamoto, K. and Sakai, M., *Macromolecules* (in press).
9. Shimada, S., Suzuki, A., Sakaguchi, M. and Hori, Y., *Macromolecules*, 1996, **28**, 973.
10. Sakaguchi, M. and Sohma, J., *J. Polym. Sci. Polym. Phys. Ed.*, 1975, **13**, 1233.
11. Kurokawa, N., Sakaguchi, M. and Sohma, J., *Polym. J.*, 1978, **10**, 93.
12. Sakaguchi, M. and Sohma, J., *J. Appl. Polym. Sci.*, 1978, **22**, 2915.
13. Hori, Y., Shimada, S. and Kashiwabara, H., *J. Phys. Chem.*, 1986, **90**, 3037.
14. Heinzer, J., *Mol. Phys.*, 1971, **22**, 167.
15. Györ, M., Rockenbauer, A. and Tüdös, F., *Macromolecules*, 1987, **20**, 3083.
16. Yamamoto, K., Shimada, S., Masato, S. and Tsujita, Y., *Polymer J.*, 1997, **29**, 370.
17. Wall, F. T., *J. Chem. Phys.*, 1943, **11**, 67.
18. Heller, C. and McConnell, H. M., *J. Chem. Phys.*, 1960, **32**, 1535.
19. Kasai *et al.*[23] reported the anisotropic hfs constants, $A'_x = 2.20$, $A'_y = 3.50$, and $A'_z = 1.20$ and $A'_{\mathrm{iso}} = 2.30\,\mathrm{mT}$, for a chain end alkyl radical. It is well-known that the isotropic value is proportional to spin density at C_α. Then, the anisotropic A values are calculated from the $A_i = A'_i \times (A_{\mathrm{iso}}/A'_{\mathrm{iso}})$, where $i = x, y, z$. The calculated values of $A_x = 1.43$, $A_y = 2.28$, and $A_z = 0.78$ mT are very similar to the assuming values ($A_x = 1.43$, $A_y = 2.33$, and $A_z = 0.72\,\mathrm{mT}$) for the simulated spectrum (broken line) in *Figure 3B*.
20. Kamachi, M. and Kajiwara, A., *Macromolecules*, 1996, **29**, 2387.
21. Fessenden, R. W. and Schuler, R. H., *J. Chem. Phys.*, 1963, **39**, 2147.
22. Matsuoka, S., *Relaxation Phenomena in Polymers*, Ch. 2. Oxford University Press, New York, 1992.
23. Kasai, P. H., *J. Am. Chem. Soc.*, 1990, **112**, 4313.