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Molecular Motion of Isolated Single Polymer Chains Tethered on a Fresh Surface of Poly(tetrafluoroethylene)

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ABSTRACT: Polyethylene, polypropylene, polybutadiene, polyisobutylene, and poly(methyl methacrylate) tethered on a fresh surface of poly(tetrafluoroethylene) were produced by a block copolymerization of PTFE with their monomers in vacuum at 77 K. The tethered polymer chains can be regarded as isolated from other tethered chains because of an extremely low fraction of the tethered chains. We call them "isolated polymer chains". A molecular mobility of tethered polymer chains was studied by electron spin resonance (ESR) using a peroxy radical at the chain end as a label. Temperature-dependent ESR spectra of the peroxy radicals were successfully observed and the ESR spectra were composed of two spectra arising from two kinds of peroxy radicals, A-radical and B-radical, which were a rigid radical due to a train conformation and a mobile radical due to a tail conformation of tethered chains, respectively. The remarkable change with anisotropic *g* values of the peroxy radicals was analyzed by computer simulation. The train−tail transition temperature where the ratio of fractional amount of B-radical reached 50% was found to linearly increase with an increase in a conformer size related to a characteristic free volume of isolated polymer chains. Moreover, the flexibility of isolated polymer chains is dependent on the number of double bonds in the main chain and the size of side chain.

Introduction

Many investigations on the molecular motion of polymer chains in the solid state or in solution have been reported. In these systems, the molecular mobility of polymer chains strongly depends on the surroundings. The mobility of the chains in the solid state depends on the free volume related to the inter- and intrapolymer chain interactions. 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 of polymer surface than that in the bulk.[1−4] Thus, the mobility is a function of intermolecular and intramolecular interactions. It is important to evaluate individually the interactions and elucidate the fundamental physical properties of the individual polymer chain.

Matsuoka et al.[5] developed a model for intermolecular cooperativity in conformational relaxation. They suggested that the smallest segmental unit of rotation (called a conformer) was surrounded by other conformers in a solid or molten state and that, in order for a conformer to completely undergo a rotational relaxation, its neighbors must also move cooperatively. A conformer can change its conformational state under such restrictions only when its close neighbors cooperate with it.

In an isolated polymer system, the above restrictions can be swept aside since intermolecular interaction (intermolecular cooperative motion) disappears. Isolated single polymer chains can be expected to have different physical properties from bulk polymer chains. We have produced some isolated single polymer chains in vacuum, in which there is a large space around the chains and their aggregation behavior is inhibited.

In our previous papers, the chain-end alkyl radical, $-CH_2CH_2^{\bullet}$, of isolated polyethylene (PE)[6−8] and the chain-end allyl radical, $-CH_2CH{=}CHCH_2^{\bullet}$, of isolated polybutadiene (PBD)[9] tethered on a fresh surface of poly(tetrafluoroethylene) (PTFE) have high mobility even at 77 K. The peroxy radicals at the end of isolated PE chains tethered on the PTFE surface also have high mobility.[10] This high mobility was interpreted in terms of the following: (1) the PE and PBD molecules were present in an extremely low segmental density on the PTFE surface in vacuum; (2) the PE and PBD chains are prevented from their aggregation because one end of the chain is tethered on the PTFE surface, and PE and PBD are immiscible with PTFE. We have reported that the isolated PE and PBD chains have an extremely higher mobility than bulk chains.

In this paper, we produced some isolated polymer chains tethered on the PTFE surface in order to observe the intrinsic molecular motion of the individual polymer chains. The molecular weights and the segmental concentrations of the tethered polymer chains were characterized. The mobility of the tethered polymer chains was studied by ESR spectroscopy using the chain end peroxy radical labeling. It is difficult to compare directly each molecular mobility of isolated chains when a chemically different propagating radical is used as a label. Using the same peroxy radical labeling makes it possible to directly compare each mobility of isolated chains at the chain end. This labeling also makes it possible to observe a molecular motion in a wider temperature range than propagating radical labeling does. We will discuss the structure and molecular mobility of the isolated polymer chains tethered on the PTFE surface, related to the degree of cooperativity proposed by Matsuoka et al.[5]

Experimental Section

Materials. PTFE powder (Fluon G163, Asahi Glass, Co., Ltd.) was used without further purification. Ethylene, propylene, isobutylene (Takachiho Co., Ltd.), and 1,3-butadiene (Tokyo Chemical Industry, Co., Ltd.) were purified by a freeze−pump−thaw method. Methyl methacrylate (MMA)-(Nacalai Tesque, Inc.) monomer was purified as usual.

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Table 1. Characteristics of Samples

sample	fraction of tethered chains (wt%)	av deg of polymerization	method
PTFE/PE/O_2			
PTFE/PBD/O_2	0.032	52	spin labeling
PTFE/PP/O_2			
PTFE/PIB/O_2	0.060	95	pyrolysis
PTFE/PMMA/O_2	0.099	88	pyrolysis

Sample Preparation. The polymer chains tethered to the fresh surface of PTFE in vacuum were produced as follows: The PTFE powder (1.50 g) was mechanically fractured with these vinyl monomer (ca. 5.0×10^{-4} mol except for MMA, ca. 2.7×10^{-5} mol) at 77 K in vacuum by a homemade vibration glass ball mill.[11] The ball milling of PTFE powder produces PTFE mechano radicals[11] trapped on the fresh surface.[12] The PTFE mechano radicals can initiate a radical copolymerization[13] of the vinyl monomer at 77 K when the PTFE radicals come into contact with the monomer by a physical mixing during the milling. Then, polymer chains tethered on the PTFE fresh surface are produced. The polymer chains have an unpaired electron at the chain end. After the copolymerization, the ESR tube connected to the glass ball mill was placed in liquid nitrogen and the powder sample was dropped into the ESR tube by turning the glass ball mill upside down.

In order to eliminate the residual monomer which did not react, the ESR tubes containing the sample were connected to a vacuum line held at 77 K and then soaked in methanol at ca. 20 K higher than the melting point of the respective vinyl monomers. We confirmed in advance that the ESR spectral intensity of each propagating radical did not decay at that temperature. The residual monomers were subsequently evacuated as much as possible for an hour under a pressure below 10^{-4} Torr.

After the residual monomer were eliminated and the propagating radicals of these monomer were observed, oxygen molecules at a pressure of 20 Torr were introduced into the sample. By annealing of the samples at the required temperatures for 15−30 min, the polymer chain ends tethered to the surface were labeled with peroxy radicals. These samples were coded as PTFE/PE/O_2, PTFE/PBD/O_2, PTFE/PP/O_2, PTFE/PIB/O_2, and PTFE/PMMA/O_2 for the samples of tethered PE, PBD, polypropylene (PP), polyisobutylene (PIB), and poly(methyl methacrylate) (PMMA) chains, respectively.

ESR Measurements. ESR spectra were observed at a low microwave power level to avoid power saturation and with 100 kHz field modulation using JEOL JES-FE3XG and 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 the well-known splitting constants of Mn^{2+} in MgO.

Spectral Simulation. The computer simulation developed by Hori et al.[14] was carried out in order to obtain several spectral parameters and to confirm the coexistence of two kinds of peroxy radicals, A-radicals and B-radicals, which were rigid and mobile radicals, respectively. The quantities determined were anisotropic g values, g_1, g_2, and g_3 ($g_1 < g_2 < g_3$) for the A-radical and g_1', g_2', and g_3' ($g_1' < g_2' < g_3'$) for the B-radical, the fractional amount of B-radical, and the line width. The line shape function was assumed to be Gaussian, and line widths were also assumed to vary linearly with the inversion of the g value.

Results and Discussion

Characterization of the Tethered Chain. We quantitatively estimated the tethered polymer fraction ($100 \times$ tethered chains (g)/(tethered chains (g) + PTFE (g)) (%) of the samples. The estimated fractions of tethered polymer are listed in Table 1. The fraction of tethered polymer chains for PTFE/PIB/O_2 and PTFE/PMMA/O_2 specimens was determined[3] by a pyrolysis. For a PTFE/PBD/O_2 specimen, the PBD fraction was determined by a spin labeling method,[15] in which the spin-labeling reagent reacts the double bond in the PBD chain. For a PTFE/PE/O_2 and PTFE/PP/O_2 specimens, the fraction of the tethered chains cannot yet be characterized. It is difficult to detect clearly degradation fractions of PE and PP by pyrolysis because the degradation temperatures of PE and PP are only ca. 100 K different from that of PTFE. Because ethylene and propylene monomers have a lower reactivity for radical polymerization than 1,3-butadiene and MMA, the fraction of the tethered chains for PTFE/PE/O_2 and PTFE/PP/O_2 can be considered to be an extremely low.

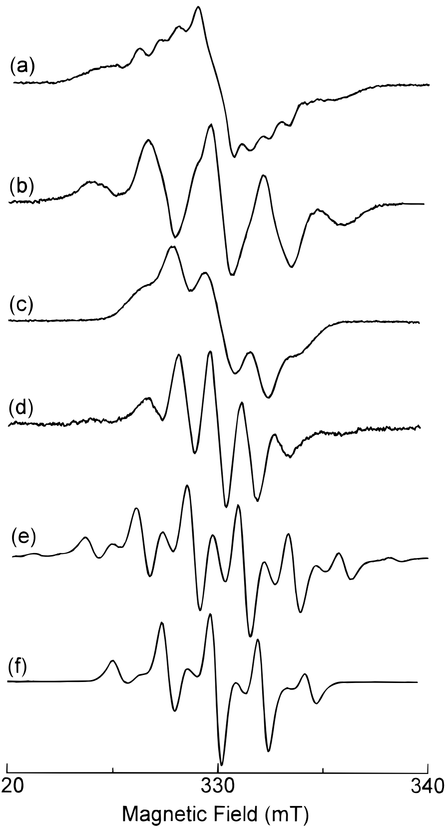

Figure 1. ESR spectra of PTFE mechanoradicals and propagating radicals of isolated single chains tethered on the PTFE surface observed at 77 K: (a) PTFE mechanoradicals and (b) PE, (c) PBD, (d) PP, (e) PIB, and (f) PMMA propagating radicals.

The average degree of polymerization of these tethered chains was calculated from the tethered point concentration (6.8×10^{16} spins/g)[7] (Table 1) and the fraction of tethered polymer chains. The area per tethered point on the PTFE surface (3100 Å^2/spin)[7] was deduced from the concentration of tethered point and the specific surface area (2.1 m^2/g)[7] of PTFE powder. As described in our previous papers,[3,9] the tethered polymer chains have no contact with the neighbor chains. Thus, these polymer chains can be regarded as isolated from other tethered chains, and we call them “isolated polymer chains”.

Oxidation of Chain End Propagating Radicals. Figure 1 shows the ESR spectra observed at 77 K for respective samples after eliminating the residual monomer. The ESR spectrum (a) is due to the PTFE mechanoradicals (main-chain scission type) after the PTFE powder is fractured without any monomer.[11] No signal due to the PTFE mechano radicals is observed in the other spectra b−f, which are identified with the spectra arising from the propagating radicals of the

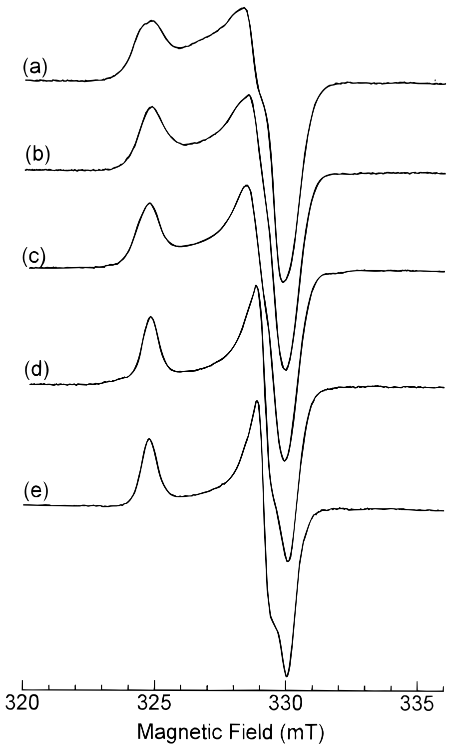

Figure 2. ESR spectra of peroxy radicals of isolated single chains tethered on the PTFE surface observed at 77 K for (a) PTFE/PE/O_2, (b) PTFE/PBD/O_2, (c) PTFE/PP/O_2, (d) PTFE/PIB/O_2, and (e) PTFE/PMMA/O_2 specimens.

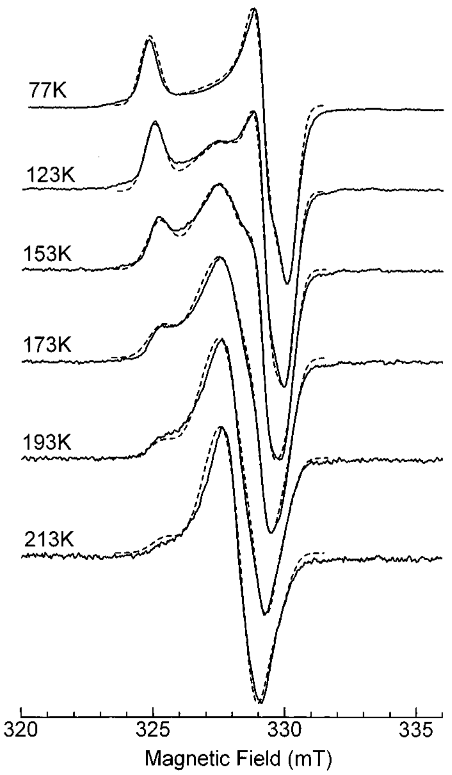

Figure 3. Temperature-dependent ESR spectra of peroxy radicals of PTFE/PIB/O_2, specimen as an example. The simulated spectra are shown with broken lines.

respective polymer chains; the spectra b and c arise from PE[6-8] and PBD propagating radicals.[9,16] The septet spectrum (d) is considered to be due to PP propagating radicals. The octet−septet spectrum (e) is due to PIB propagating radicals. This spectrum should be interpreted by assuming two stable conformations as well as PMMA[17] radicals. The quintet−quartet spectrum (f) is typical for propagating radicals of the methacrylic derivative, and this is due to PMMA propagating radicals.[17] Thus, the ESR spectra are found to be attributed to only propagating radicals which remain even after eliminating the residual monomer.

The peroxy radical labeling experiments were performed by a reaction of the propagating radicals with oxygen molecules as described in the Experimental Section. Figure 2 shows the ESR spectra of the peroxy radicals at the chain end of the respective polymer chains observed at 77 K. Each peroxy radical labeling is found to be successful because of the absence of any signal due to the propagating radical of the respective polymer chains in these spectra.

Characteristics of ESR Spectra of Peroxy Radicals. Figure 3 shows the temperature dependence of the observed ESR spectra (solid lines) of the PTFE/PIB/O_2 specimen. The ESR spectral change is attributed to a temperature dependence of the molecular motion of the tethered chains. Schlick et al. interpreted the temperature dependent ESR spectra of peroxy PE and PTFE in terms of g-anisotropy averaging of one radical.[18,19] The ESR spectra observed in our experiments are different from that calculated assuming the cubic-jump model,[19] 90 and 180° jumps of the OO fragment rotation about the CO bond, or 60, 120, and 180° jumps about the chain axis as a function of the rate of interconversion between sites. In addition, Hori et al. evidenced an existence of two components of isotactic-PP peroxy radicals based on the decay reaction of the radicals.[20] Therefore, in our case, the spectral simulation was carried out by assuming two components of peroxy radicals. The broken lines show the simulated spectra, which consisted of two components. The spectra of all samples also comprised two components. One, which we will call the A-radical, is similar to the amorphous patterns of the peroxy radicals; the other, called the B-radical, is a broad singletlike pattern caused by more averaged g values. That is, A-radical and B-radicals are rigid and mobile radical, respectively. A-radical (immobile radical) converts to B-radical (mobile radical) when a characteristic free volume which depends on polymer species is produced. For instance, when the volume of vacancy between the tethered chains and PTFE surface exceeds the characteristic free volume V_r, the mobile component due to the B-radical can be observed. When the segmental concentration of the tethered chains is extremely low, the tethered chains take a mushroomlike structure[21,22] or a train structure[23,24] strongly adsorbed on the surface at very low temperature. The mobility of both structures is restricted. Since the average degree of polymerization of tethered chains here is not so high, the tethered chains are considered to take a train conformation at very low temperatures. In contrast, the tethered chains take a mobile tail[23,24] structure protruding from the surface at higher temperature because of a low segmental concentration. The motion of the tethered chains was concluded to be a three-dimensional reorientation because the singletlike spectra were observed at higher temperature. This motion requires a large space around the chains in comparison with the rigid chain. Therefore, A-radical and B-radical can be considered to reflect the tethered chains of train and tail conformations, respectively, as schematically shown in Figure 4. Thus, a fractional amount of train and tail conformation can be determined quantitatively.

Figure 4. Schematic illustration of tethered polymer chains on the PTFE surface, which take train conformations at an extremely low temperature (A) and tail conformations at higher temperatures (B).

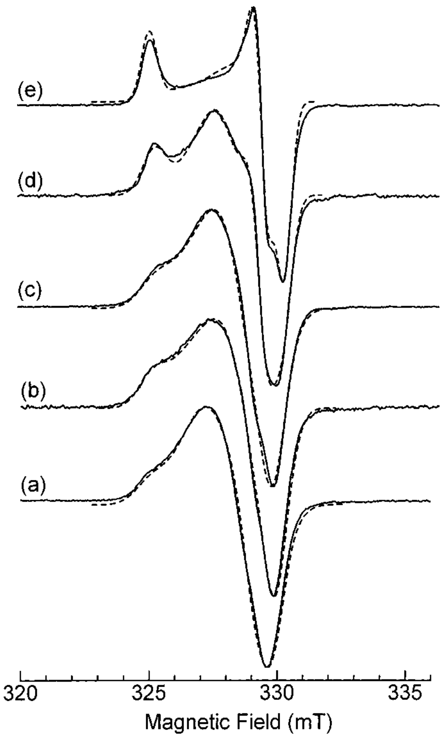

Figure 5. ESR spectra of peroxy radicals of isolated single chains tethered on the PTFE surface observed at 153 K for (a) PTFE/PE/O_2, (b) PTFE/PBD/O_2, (c) PTFE/PP/O_2, (d) PTFE/PIB/O_2, and (e) PTFE/PMMA/O_2 specimens. The simulated spectra are shown with broken lines.

When the tethered polymer chains have the tail conformation, the space around the chains is very large and a high molecular mobility of the single tethered chain can be observed. The flexibility of the tethered polymer chains having the tail conformation can be elucidated by estimating an extent of motionally averaging of anisotropic *g* values with temperature.

Structure and Molecular Motion of the Peroxy Radical of Isolated Single Polymer Chains Tethered on the PTFE Surface. (a) Conformational Transition of Tethered Chains. The spectral simulation was carried out to obtain spectral parameters assuming the coexistence of two kinds of peroxy radicals having different mobility. Figure 5 shows the ESR spectra for the various samples observed at 153 K (solid lines). The simulated spectra are also shown with broken lines. The agreement between the observed and simulated spectra is excellent. At other temperatures, the simulated spectra were also in good agreements with the observed spectra. From the spectral simulations in Figure 5, the fractional amount of B-radical (mobile radical) at 153 K were estimated as 67, 56, 55, 35, and 11% for PTFE/PE/O_2, PTFE/PBD/O_2, PTFE/PP/O_2, PTFE/PIB/O_2, and PTFE/PMMA/O_2 specimens, respectively.

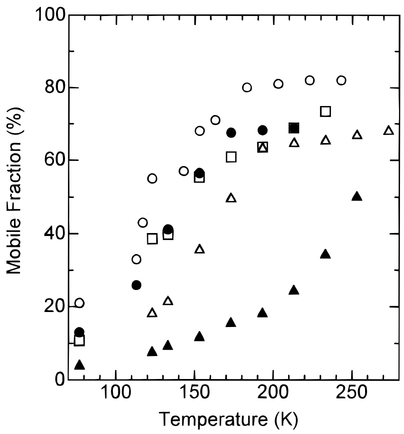

Figure 6. Temperature dependence of a mobile fraction for PTFE/PE/O_2 (open circle), PTFE/PBD/O_2 (solid circle), PTFE/PP/O_2 (square), PTFE/PIB/O_2 (open triangle), and PTFE/PMMA/O_2 (solid triangle) specimens.

Figure 6 shows the temperature dependencies of fractional amounts of B-radicals (mobile radicals). The mobile fraction gradually increases in a low-temperature range and steeply increases at a certain temperature for all samples with an increase in temperature. This is regarded as one transitional phenomenon. In general, the tethered chains at extremely low temperature take a train conformation having the "occupied" volume V_0 on the PTFE surface. When the tethered chains get a thermal energy and obtain a characteristic free-volume V_r, they begin to protrude from the PTFE surface and take a tail conformation as shown Figure 4. This transition is regard as a train−tail transition. In other words, when a "train" segment has the thermal energy equal to the segment−PTFE interaction energy, its segment converts to a "tail" segment. The energy is extremely low in comparison with the segment−segment interaction energy in the homopolymer bulk, and then the transition occurs at a low temperature. A temperature where the fractional amount of mobile radicals reaches 50% is defined as a conformational transition temperature T_r (train−tail transition). From Figure 6, the T_rs are found to be 123, 142, 145, 174, and 253 K for PTFE/PE/O_2, PTFE/PBD/O_2, PTFE/PP/O_2, PTFE/PIB/O_2, and PTFE/PMMA/O_2 specimens, respectively. These transition temperatures are much lower than T_gs for the respective homopolymers.

(b) Relationship between Conformational Transition Temperature and Conformer Size. Matsuoka et al.[5] proposed a domain where the number (*z*) of conformers moved cooperatively. If equilibrium can be achieved at a low-temperature limit T_0, every conformer becomes meshed with all others and the number of conformers in one domain is nearly infinite. At the high-temperature limit they called T^*, on the other hand, each conformer can relax independently from neighbors, and then the number of conformer in each domain is 1. Between the two extreme temperatures, the size of a domain is specified by *z* in the domain which is a measure of the degree of cooperativity of molecular motion.

Matsuoka et al.[5] defined also a conformer size *M* as molecular weight M_w of monomer unit divided by the number (N_c) of conformer in the unit.

The conformer size of polymer chain is related to the characteristic free-volume where the transition of the isolated chain can occur. The train−tail transition occurs when the tethered polymer chains have the characteristic free volume. We will discuss the molecular motion of isolated polymer chains tethered on the

Table 2. Relationship between Transition Temperature and Conformer Size[a]

sample	T_r (K)	M_r	T_g (K)	M
PTFE/PE/O_2	123	(28 + 32)/(2 + 1)	163	28/2
PTFE/PBD/O_2	142	(54 + 32)/(3 + 1)	218	54/3
PTFE/PP/O_2	145	(42 + 32)/(2 + 1)	243	42/2
PTFE/PIB/O_2	174	(56 + 32)/(2 + 1)	199	56/3.5
PTFE/PMMA/O_2	253	(100 + 32)/(2 + 1)	378	100/2

[a] Conformer sizes M_r and M are molecular weight M_w of monomer unit divided by number of conformer in the unit for isolated and bulk polymer system, respectively.

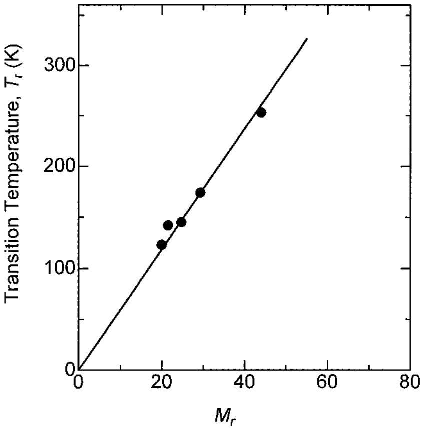

Figure 7. Train−tail temperature (T_r) vs conformer size as described in Table 2.

PTFE surface using a conformer size proposed by Matsuoka et al.[5].

Table 2 indicates the train-tail transition temperatures (T_r), the average conformer sizes M_r of the peroxy radicals in the present paper, and glass transition temperatures (T_g) of the homopolymer bulk.[5] One conformer due to the oxygen molecule of the peroxy radical should be added to the number of conformers proposed by Matsuoka et al.[5] for the calculation of the conformer size of the chain end peroxy radical. In our case, the additions of 1 for N_c and 32 for M_w were made to obtain M_r. Matsuoka et al.[5] suggested that the methyl groups took part in the conformational changes in the case of PIB because the extremely crowded structure of PIB was considered to require its rotation to accompany the unkinking relaxation of the main-chain backbone. Therefore, in the case of PIB, the number of conformers was reported to be 3.5. However, in this study, two conformers in the repeat unit must be taken because isolated PIB chains have no crowded structure. The train-tail transition temperatures T_r are plotted against the average conformer size M_r in Figure 7. The transition temperature is clearly found to be a linear function of M_r, which is very different from the relationship between T_g and conformer size in the homopolymer bulk. The relaxation of isolated polymer chains is concluded to be also related to their average conformer size.

The difference between the enthalpy at 0 K and that at T_g, $E_h(=T_gS_{cg})$ per mole can be given as follows:

$$E_h = T_g S_{cg} = \frac{\Delta V_g}{V_g}\left(\frac{\Delta C_p}{\Delta\alpha}\right)_{T_g} \tag{1}$$

The above E_h has been designed as "hole energy" by Kanig,[25] since it is the energy required to create the free volume fraction $f_g = \Delta V_g/V_g$ at T_g, where S_{cg} is the conformational entropy at T_g, ΔV_g is the free volume at T_g, ΔC_p is the difference between the specific heat at in glass and that in liquid, and $\Delta\alpha$ is the difference between thermal expansion coefficient in glass and that in liquid.

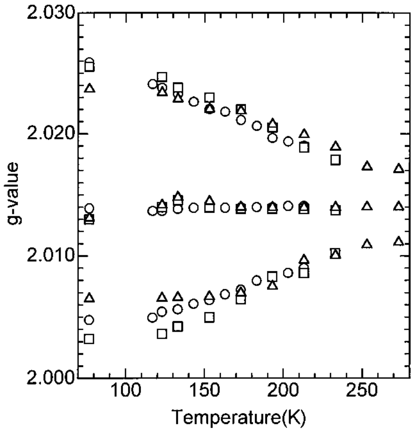

Figure 8. Changes of anisotropic *g* values of peroxy B-radicals for PTFE/PE/O_2 (circle), PTFE/PP/O_2 (square), and PTFE/PIB/O_2 (triangle) specimens.

Equation 1 is modified for the isolated polymer chain system. The hole energy $E_h'(=T_rS_{cr})$ per mole of conformer corresponds to the cohesive energy per mole between tethered chains and PTFE

$$E_h' = T_r S_{cr} = \frac{\Delta V_r}{V_r}\left(\frac{\Delta C_p}{\Delta\alpha}\right)_{T_r} \tag{2}$$

where S_{cr} is the conformational entropy at the train−tail transition temperature, T_r. The cohesive energy per mole of conformer is required to create the free-volume fraction $f_r = \Delta V_r/V_r$ at T_r. Equation 2 is modified by using the value of $\Delta C_p/\Delta\alpha$ per gram, $(\Delta C_p/\Delta\alpha)_{g,\,Tr}$ which is independent of T_r.[5]

$$E_h' = T_r S_{cr} = \frac{\Delta V_r}{V_r}\left(\frac{\Delta C_p}{\Delta\alpha}\right)_{g,T_r} M_r \tag{3}$$

Assuming S_{cr} and free volume fraction $\Delta V_r/V_r$ are independent on conformer size and T_r in this study, we can obtain

$$T_r \propto M_r \tag{4}$$

The assumption holds good when molecular motion has no cooperativity (the number *z* of the conformer in the domain is 1). Therefore, the liner relationship in the Figure 7 also reflect the isolated chains tethered on PTFE surface.

(c) Flexibility of the Isolated Single Polymer Chain. The changes of anisotropic *g* values of B-radicals (mobile) reflect a molecular motion of tail segments of polymer chain having a large free space around the chain. Therefore we can discuss each flexibility of an isolated single polymer chain.

Figure 8 shows the change of anisotropic *g* values of B-radicals for PTFE/PE/O_2, PTFE/PP/O_2, and PTFE/PIB/O_2 specimens with temperature. Each flexibility of PE, PP, or PIB is expected to be different. But each trace of the *g* value changes is almost the same. That is, the peroxy radical labeling cannot detect the difference of flexibility among PE, PP, and PIB. In other words, the motion of the methyl groups of side chain do not affect the motional averaging of *g* values of peroxy radical. This is a reflection that their is no role that

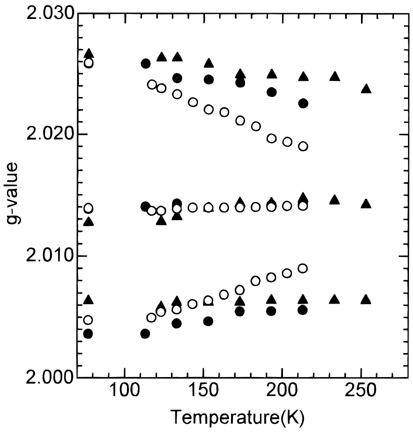

Figure 9. Changes of anisotropic *g* values of peroxy B-radicals for PTFE/PE/O_2 (open circle), PTFE/PBD/O_2 (solid circle), and PTFE/PMMA/O_2 (solid triangle) specimens.

the methyl group in isolated PIB chains plays in the flexibility, and then two conformers in the repeat unit must be taken for the isolated PIB chains as mentioned in the previous section.

Figure 9 shows the changes of anisotropic *g* values of mobile radicals for PTFE/PE/O_2, PTFE/PBD/O_2, and PTFE/PMMA/O_2 specimens with temperature. The extent of the *g* value change for the tethered PMMA chains is the smallest and that for the PBD chains is in the middle in three specimens. The size of the methyl ester side chain is larger so that the large side chain restrains the rotation (flexibility) around the main chain of PMMA. The PBD chains do not have side chains but double bonds in a main chain. The double bonds restrict the rotation around the main chain. From Figures 8 and 9, the extent of change of *g* values for PBD chains is smaller than that for PE, PP, and PIB chains. The flexibility of these polymer chains is proved to be affected by double bonds rather than by methyl groups of the side chain.

Thus, the flexibility of isolated single polymer chains depends on the presence of a double bond in the main chain and the size of the side chain.

Noncooperative Motion of the Propagating Radical of the Isolated Polybutadiene Chain on the PTFE Surface. Figure 10 shows the transition map, log frequency vs $1/T$ (K^{-1}), for polycarbonate (PC),[5] poly(ethylene terephthalate) (PET),[5] and isolated PBD.[9] Matsuoka et al.[5] reported that the domain size z_g at T_g is typically ca. 7−10 conformers and the number of conformers in the β process must be equal to or smaller than the domain size for the α process at T_g. The size of a unit of relaxation for the β process is between 2 and 3 conformers for PC and 4 or 5 conformers for PET, as shown in Figure 10. One point shown on the straight line marked $z = 1.2$ corresponds to the frequency and the temperature of the methyl group rotation in polyethylene chains.[5]

We have studied a site-exchange motion between two equilibrium conformations of propagating radicals of isolated PBD chains tethered on a PTFE surface and reported the apparent activation energy of 2.5 kcal/mol.[9] The frequencies and the temperatures of the site-exchange motion of the propagating radical of the isolated PBD chains are also plotted in Figure 10 with solid circles. This frequency of the site-exchange motion is higher than that of the methyl group rotation. Matsuoka et al.[5] reported that the methyl group rotation was a good example of the unhindered conformer; i.e. the domain size $z = 1.2$. However, we think the domain size *z* of isolated PBD chains is nearly equal to 1 and it is a better example of the unhindered conformer.

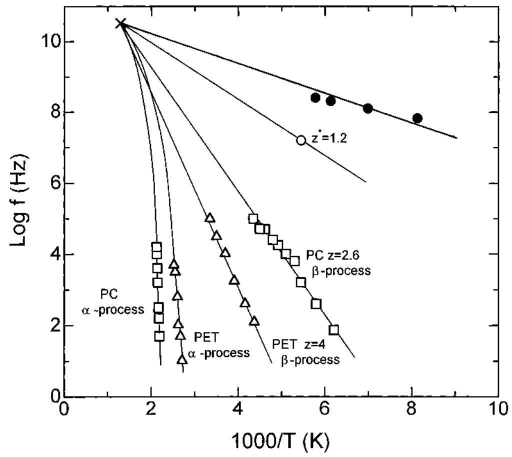

Figure 10. Transition map−log frequency where the dielectric loss maximum vs $1/T$ (K^{-1}) for PC and PET. The star mark represents a relaxation time at $T^* = 773$ K (data from ref. 5) The frequencies of the site-exchange motion of propagating radical of isolated PBD chains are shown with solid circles (data from ref 9).

Thus, the propagating radicals of isolated PBD chains tethered on the PTFE surface can be considered to have noncooperative motion.

Conclusion

Mechanical fracture of PTFE powder with several monomers produced some isolated polymer chains tethered on a PTFE fresh surface in a vacuum. Peroxy radical is very easily formed at the polymer chain ends, and its labeling is useful to compare each molecular motion of polymer having different chemical structures and to observe the motion in the wide temperature range. We could elucidate the molecular structure and the molecular motion of isolated single polymer chains.

The train-tail transition temperature where a fractional amount of B-radicals (mobile radicals) reached 50% was defined. The transition temperature of isolated single polymer chains was clearly found to be a linear function of its conformer size proposed by Matsuoka et al. Moreover, the flexibility of isolated single polymer chains is proved to be affected by the presence of a double bond in the main chain rather than by only one or two methyl groups of the side chain. The flexibility also depends on size of the side-chain.

The temperature dependence of motional frequency of a propagating radical of isolated PBD chains indicates that the number of conformers which move cooperatively in the domain is equal to 1.

Isolated polymer chains tethered on the PTFE surface can be concluded to move noncooperatively.

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