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A Thermodynamic Study on Molecular Motion of the Peroxide Ends of Isolated Single Polymer Chains Tethered to the Surface of Poly(tetrafluoroethylene) in Vacuo

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ABSTRACT: A thermodynamic study on the molecular motion of peroxide ends of isolated single polymer chains tethered to the surface of poly(tetrafluoroethylene) (PTFE) in vacuo is discussed. The five kinds of isolated single polymer chains were produced by a block copolymerization of PTFE with five kinds of monomers at the PTFE surface in vacuo. Copolymerized polyethylene (PE), polypropylene (PP), polyisobutylene (PIB), polybutadiene (PBD), and poly(methyl methacrylate) (PMMA) have radicals at the free ends of their chains. The end radicals were converted to peroxide radicals by contact with oxygen. The peroxide radicals were used as labels for detecting the molecular motion of the peroxide ends of isolated single polymer chains tethered to the PTFE surface in vacuo. A "train−tail" (immobile−mobile) transition of the peroxide ends of the isolated single polymer chains was analyzed using a new model in which the motional relaxation is due to the rotational relaxation of a "rotmer". The rotmer is the smallest rotational unit in the repeat unit forming an isolated single polymer chain and has a reduced molecular weight (M_{ro}). If the ratio of a population of freely rotating rotmers in the tail state to that of frozen rotmers in the train state can be expressed by Boltzmann statistics with transition free energy (ΔG), the transition enthalpy (ΔH_{ro}) and the transition entropy (ΔS_{ro}) of rotmers due to the train−tail transition can be estimated. These thermodynamic values and their linear relationships among ΔH_{ro}, transition temperature (T_{ro}), and M_{ro} were found. In contrast, ΔS_{ro} was constant in relation to both T_{ro} and M_{ro}. These relationships were interpreted to mean that the rotmers, which form isolated single polymer chains, are free from the neighboring rotmers which form neighboring isolated single polymer chains.

Introduction

Many studies on the molecular motion of polymer chains in the solid state have reported that chain mobility is strongly affected by the surroundings. The molecular motion of a chain in the bulk is induced by the production of a certain size of free volume which is formed by the cooperative motion of some segmental units. Matsuoka et al.[1] proposed a cooperative domain model for a motional relaxation of chains in the bulk. A domain in a solid or a molten state is surrounded by several other domains. Each domain is composed of several of the smallest segmental units (called conformers). In order for a domain to complete a relaxation, the conformers in the domain must also move in cooperation. A relaxation function is formulated based on a size distribution of the domain that is composed of several conformers. Matsuoka's model was used to explain several universal aspects of the relaxation phenomena in bulk polymers. In contrast, in an isolated single polymer chain system, segmental relaxation may not require interconformer cooperation and may complete a relaxation with only a conformer independently.

In our previous papers, we reported that the ends of isolated polyethylene (PE)[2−4] and polybutadiene (PBD)[5,6] chains tethered to a fresh surface of poly(tetrafluoroethylene) (PTFE) in vacuo have high mobility even at 77 K. This high mobility was indicated by measurements with an electron spin resonance (ESR) spectrometer and by their spectral simulations. In particular, the ends of isolated PE chains tethered to the PTFE surface in vacuo cause a site exchange motion at 15 K.[3,4] The high mobility was interpreted in terms of the followings: (1) a tethered PE or PBD chain is isolated from neighboring tethered polymer chains; (2) the tethered polymer chains are prevented from aggregating because one end of each chain is tethered to the PTFE surface with a covalent bond; and (3) the tethered polymer chains are immisible with PTFE. In these systems, however, the mobility of the ends of isolated sinlge polymer chains could not be directly compared with the results of ESR measurements. Each isolated polymer chain has a different radical structure. Consequently, a different ESR spectrum and a different mode of molecular motion are observed. On the other hand, it is well-known that ESR spectra of the peroxide radical with any different polymer structure are identical to each other when the molecular motion is identical.[7−10] In our previous paper,[11] we reported that the peroxide radicals at the end of isolated PE,[12] polypropylene (PP), PBD, polyisobutylene (PIB), and poly(methyl methacrylate) (PMMA) chains tethered to the PTFE surface also have high mobility. Mobile fractions of the peroxide radical were plotted against the observation temperature, and the transition temperatures of a "train−tail" (immobile−mobile) transition were obtained by such plots. The results indicated that the transition temperatures were proportional to the size of the conformer. This proportionality was explained by the concept of the creation of a characteristic free volume, in which the transition entropy was assumed to be independent of both the transition temperature and the size of the mobile unit. These assumptions were introduced into

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the analysis without corresponding data. Furthermore, the thermodynamic values of the train-tail transition could not be deduced by the free-volume theory in the previous paper.[11]

We propose a novel model ("rotmer model") for the analysis of the molecular motion of the peroxide ends of isolated single polymer chains tethered to the PTFE surface in vacuo. Their thermodynamic values can be estimated by such a model. The rotmer model is based on two ideas. One is that a motional relaxation of the peroxide ends of the isolated single polymer chains in vacuo is due to the rotational relaxation of a "rotmer", which is the smallest rotational unit in the repeat unit forming an isolated single polymer chain. The other is that the train−tail transition of the peroxide ends is due to a transition from literally frozen rotmers (train state) to freely rotating rotmers (tail state) and that the populations of freely rotating rotmers and frozen rotmers can be shown with Boltzmann statistics. By this rotmer model, the transition enthalpy (ΔH_{ro}) and transition entropy (ΔS_{ro}) can be deduced, and the relationships among ΔH_{ro}, ΔS_{ro}, transition temperature (T_{ro}), and reduced molecular weight (M_{ro}) of rotmers can be discussed. Furthermore, this confirms the assumption in our previous paper,[11] i.e., that transition entropy is independent of both transition temperature and the size of the conformer which is related to M_{ro} in our case.

Experimental Section

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 the freeze−pump−thaw method. Methyl methacrylate (MMA) (Nacarai Tesque, Inc.) was purified as usual.

The polymer chains tethered to the surfae of PTFE in vacuo were produced as follows:[11] The PTFE powder (1.50 g) was mechanically grounded with these vinyl monomers (about 5.0×10^{-4} mol except for MMA, which was about 2.7×10^{-5} mol) at 77 K in vacuo by a homemade vibration glass ball mill.[13] The ball milling of PTFE powder produces PTFE mechanoradicals[13] trapped on the fresh surface.[14] Such radicals can initiate a radical copolymerization of the vinyl monomer at 77 K when the PTFE radicals come into contact with the monomer by physically mixing during the milling. Then, polymer chains tethered to the PTFE fresh surface are produced. The polymer chains have an unpaired electron at each free end of the chain. 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 elimiate the residual monomers 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 about 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 monomers were eliminated and the propagating radicals of these monomers were observed, oxygen molecules at a pressure of 20 Torr were introduced into the sample. When the samples were annealed at the required temperatures for 15−30 min, the polymer chain ends tethered to the surface were labeled with peroxide 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, polypropyelene (PP), polyisobutylene (PIB), and poly(methyl methacrylate) (PMMA) chains, respectively.

ESR spectra were observed at a low microwave power level to avoid power saturation and with a 100 kHz field modulation using JEOL JES-FE3XG and JES-RE1XG spectrometers (X-band) coupled to an NEC PC 9801 microcomputer. 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.

The computer simulation developed by Hori et al.[15] was carried out to obtain several spectral parameters and to confirm the coexistence of two kinds of peroxide radicals, i.e., immobile peroxide radicals and mobile peroxide radicals. The quantities determined were amisotropic g-values, the fractional amount of a mobile peroxide radical. The line-shape function was assumed to be Gaussian.

Results and Discussion

We estimated the tethered polymer fraction (100 × tethered chains (g)/(tethered chains + PTFE (g)) (wt %) of the samples. The fraction of the tethered polymer of PTFE−PPBD−O_2 was estimated to be 0.032 wt % by the spin-labeling method[6] in which the spin-labeling reagent reacts with the double bond in the PBD chain. The fractions of tethered polymers of PTFE−PIB−O_2 and PTFE−PMMA−O_2 are estimated to be 0.060 and 0.099 wt %, respectively, by a pyrolysis.[11]

The average degrees of polymerization of tethered chains of PTFE−PBD−O_2, PTFE−PIB−O_2, and PTFE−PMMA−O_2 were estimated to be 52, 95, and 88, respectively.[11] These values were calculated from the tethered point concentration (6.8×10^{16} spins/g)[3] and fractions of tethered polymer chains. The area per tethered point on the PTFE surface (3.1×10^3 Å^2/spin)[3] was deduced from the concentration of tethered point and the specific surface area (2.1 m^2/g)[3] of the PTFE powder. For PTFE−PE−O_2 and PTFE−PP−O_2 samples, the fraction of the tethered chains cannot yet be characterized. It is difficult to clearly detect the degradation fractions of PE and PP by pyrolysis because the degradation temperatures of PE and PP differ by only ca. 100 K from that of PTFE. Because ethylene and propylene monomers have a lower reactivity for radical polymerization than 1,3-butadiene and MMA, the fractions of the tethered chains for PTFE−PE−O_2 and PTFE−PP−O_2 can be considered to be extremely low. The polymerization degrees of PTFE−PE−O_2 and PTFE−PP−O_2 may be lower than those of PTFE−PBD−O_2 and PTFE−PMMA−O_2. As described in our previous papers,[5,11,16] the tethered polymer chains have no contact with the neighboring tethered polymer chains. Thus, these polymer chains can be regarded as "isolated single polymer chains".

Figure 1 shows the temperature dependence of the observed ESR spectra (solid lines) of the PTFE−PIB−O_2. Hori et al. reported the existence of two components of isotropic PP peroxide radicals based on the decay reaction of the radicals.[10] Thus, in our case, the spectral simulation was carried out by assuming two components of peroxide radicals. The broken lines show the simulated spectra, which consisted of two components. The spectra of all samples were also comprised of two components. One was an immobile peroxide radical with a pattern similar to the amorphous patterns of the peroxide radicals due to frozen molecular motion. The other was a mobile peroxide radical that showed a broad singletlike pattern caused by more averaged g values due to a three-dimensional molecular motion. The immobile peroxide radical converts to the mobile peroxide radical at a certain temperature range. The number of mobile radicals increases gradually in a low-

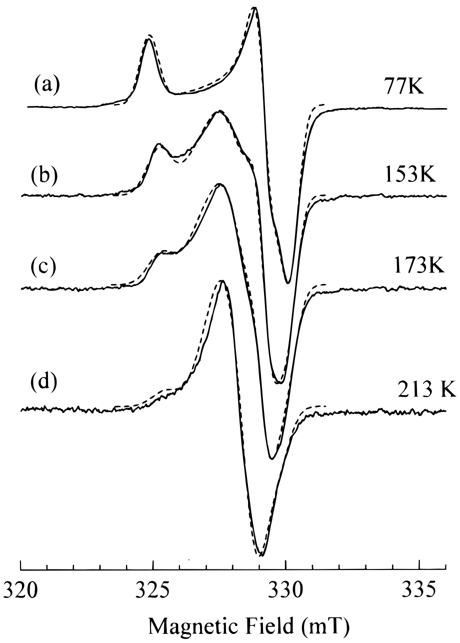

Figure 1. Temperature-dependent ESR spectra of peroxide radicals of the PTFE−PIB−O$_2$ sample as an example. The observed and simulated spectra are shown with solid lines and broken lines, respectively.

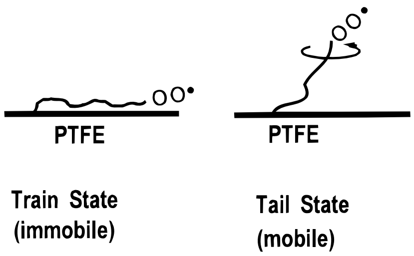

Figure 2. Schematic illustration of an isolated single polymer chain tethered to the PTFE surface in train state (immobile state) and tail state (mobile state).

temperature range and increases steeply when the temperature rises to a certain point. It is assumed that the immobile peroxide radicals assume a train structure,[17,18] in which the isolated single polymer chains tethered to the PTFE surface are adsorbed on the PTFE surface and the mobility is frozen. We called this the "train state". In contrast, the mobile peroxide radicals assume a tail structure,[17,18] in which the peroxide radicals of the isolated single polymer chains tethered to the PTFE surface protrude from the surface and rotate freely. We called this the "tail state". Figure 2 shows a schematic illustration of the isolated single polymer chains tethered to the PTFE surface in the train state (immobile state) and the tail state (mobile state).

The train fraction (F_{train}) was defined as the ratio of concentration of the immobile peroxide radicals to the total concentration, including the mobile and immobile peroxide radicals at the observation temperature. The tail fraction (F_{tail}) was defined as the ratio of concentration of the mobile peroxide radicals to the total concentration. The total concentration was normalized to unity, $F_{\mathrm{tail}} + F_{\mathrm{train}} = 1$. The F_{tail} values were estimated by spectral simulations of the ESR spectra at each observation temperature.

Figure 3 shows the temperature dependencies of F_{tail} values. Each F_{tail} of PTFE−PE−O$_2$, PTFE−PBD−O$_2$, PTFE−PP−O$_2$, PTFE−PIB−O$_2$, or PTFE−PMMA−O$_2$ gradually increases in a low-temperature range and steeply increases when a certain temperature is reached. When the F_{tail} value reached 0.5, i.e., the equal distribution of the peroxide radicals in the train state and the tail state, the temperature was defined as a transition temperature (T_{ro}) from the train state to the tail state of the peroxide radicals. The T_{ro} values were estimated 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$_2$, respectively.[11]

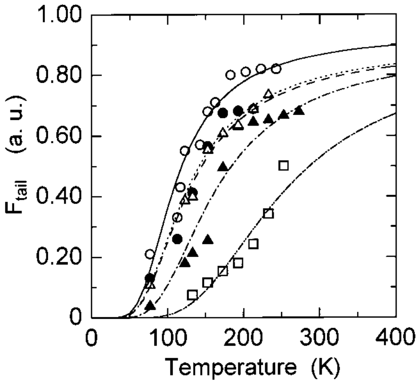

Figure 3. Temperature dependencies of F_{tail} values for PTFE−PE−O$_2$ (open circles and solid line), PTFE−PBD−O$_2$ (solid circles and broken line), PTFE−PP−O$_2$ (open triangles and dotted line), PTFE−PIB−O$_2$ (solid triangles and solid−dotted line), and PTFE−PMMA−O$_2$ (squares and solid−two dotted line). Each guideline is drawn by eq 7 in the text with ΔH_{ro} and ΔS_{ro} values.

Here, we analyze the train−tail transition of the peroxide ends of isolated single polymer chains tethered to the PTFE surface in vacuo using the rotmer model. The rotmer is a rotational part of a monomer unit and is assumed to be a rigid rotor. The rotmer has a reduced molecular weight, $M_{\mathrm{ro}} = (M_{\mathrm{m}} + M_{\mathrm{oo}})/N_{\mathrm{r}}$, where M_{m} and M_{oo} are the respective molecular weights of a monomer unit and oxygen molecule (the peroxide end) and N_{r} is the number of rotation units as the rotmer in the monomer unit. M_{ro} values of the samples are listed in Table 1.

At the energy system in the train state, the rotmers which form an isolated single polymer chain tethered to and adsorbed on the PTFE surface in vacuo are frozen. The energy system of the rotmer can be expressed as its free energy (${}^{\mathrm{train}}G$) in the train state

$$
{}^{\mathrm{train}}G = {}^{\mathrm{train}}E_{\mathrm{rot}} + {}^{\mathrm{train}}E_{\mathrm{vib}} + {}^{\mathrm{train}}E_{\mathrm{trans}} + {}^{\mathrm{train}}E_{\mathrm{rotmer-rotmer}} + {}^{\mathrm{train}}E_{\mathrm{rotmer-solv}} + {}^{\mathrm{train}}E_{\mathrm{rotmer-surf}} + {}^{\mathrm{train}}P({}^{\mathrm{train}}V) - T({}^{\mathrm{train}}S) \quad (1)
$$

where ${}^{\mathrm{train}}E_{\mathrm{rot}}$, ${}^{\mathrm{train}}E_{\mathrm{vib}}$, and ${}^{\mathrm{train}}E_{\mathrm{trans}}$ are the rotation, vibration, and translation energies of a rotmer, respectively. ${}^{\mathrm{train}}E_{\mathrm{rotmer-rotmer}}$, ${}^{\mathrm{train}}E_{\mathrm{rotmer-solv}}$, and ${}^{\mathrm{train}}E_{\mathrm{rotmer-surf}}$ are, respectively, the interaction energy between a rotmer forming an isolated single polymer chain and rotmers forming neighboring isolated single polymer chains, the interaction energy between a rotmer and solvent molecules, and the interaction energy between a rotmer and the PTFE surface. ${}^{\mathrm{train}}P$, ${}^{\mathrm{train}}V$, T, and ${}^{\mathrm{train}}S$ are the pressure, volume, temperature, and entropy of a rotmer, respectively. In contrast, at the energy system of the tail state, the rotmers, which form an isolated single polymer chain tethered to the PTFE in vacuo, protrude from the PTFE surface and are freely rotating. The energy system of the rotmer can be exhibited as its free energy (${}^{\mathrm{tail}}G$) in the tail state

$$
{}^{\mathrm{tail}}G = {}^{\mathrm{tail}}E_{\mathrm{rot}} + {}^{\mathrm{tail}}E_{\mathrm{vib}} + {}^{\mathrm{tail}}E_{\mathrm{trans}} + {}^{\mathrm{tail}}E_{\mathrm{rotmer-rotmer}} + {}^{\mathrm{tail}}E_{\mathrm{rotmer-solv}} + {}^{\mathrm{tail}}E_{\mathrm{rotmer-surf}} + {}^{\mathrm{tail}}P({}^{\mathrm{tail}}V) - T({}^{\mathrm{tail}}S) \quad (2)
$$

where the definition of each term in the tail state is identical with that in the train state except for the superscript "tail". In the low-temperature region, rotmers are followed by the energy system shown in eq 1. But in the higher temperature region, several rotmers can transfer from the energy system of the train state to that of the tail state as shown in eq 2. This transformation of rotmers from the energy system of the train state to that of the tail state can be regarded as the transition of the rotmer.

The rotmers which form isolated single polymer chains tethered to the PTFE surface in vacuo satisfy the following conditions: (i) ${}^{\mathrm{train}}E_{\mathrm{rot}}$ is neglected because the molecular motion of the rotmers forming the isolated single polymer chain in the train state is literally frozen; (ii) ${}^{\mathrm{train}}E_{\mathrm{vib}}$ and ${}^{\mathrm{tail}}E_{\mathrm{vib}}$ can be neglected because each rotmer is assumed to be a rigid rotor; (iii) ${}^{\mathrm{train}}E_{\mathrm{trans}}$ and ${}^{\mathrm{tail}}E_{\mathrm{trans}}$ are neglected because the rotmers forming the isolated single polymer chain are connected to the PTFE surface with a covalent bond; (iv) ${}^{\mathrm{train}}E_{\mathrm{rotmer-rotmer}}$ and ${}^{\mathrm{tail}}E_{\mathrm{rotmer-rotmer}}$ are neglected because rotmers forming the isolated single polymer chain are free from neighboring rotmers which form the neighboring isolated single polymer chains on the PTFE surface; (v) ${}^{\mathrm{train}}E_{\mathrm{rotmer-solv}}$ and ${}^{\mathrm{tail}}E_{\mathrm{rotmer-solv}}$ are neglected because no solvent is present in this system; (vi) ${}^{\mathrm{tail}}E_{\mathrm{rotmer-surf}}$ can be neglected because rotmers forming the isolated single polymer chain protrude from the PTFE surface in the tail state; (vii) ${}^{\mathrm{train}}P$ and ${}^{\mathrm{tail}}P$ are nearly zero because rotmers forming an isolated single polymer chains exist in vacuo. Thus ${}^{\mathrm{train}}P({}^{\mathrm{tail}}V)$ and ${}^{\mathrm{tail}}P({}^{\mathrm{tail}}V)$ are neglected. When the above requirements i–vii are applied to eqs 1 and 2, they can be simplified as

$$
{}^{\mathrm{train}}G = {}^{\mathrm{train}}E_{\mathrm{rotmer-surf}} - T({}^{\mathrm{train}}S) \quad (3)
$$

$$
{}^{\mathrm{tail}}G = {}^{\mathrm{tail}}E_{\mathrm{rot}} - T({}^{\mathrm{tail}}S) \quad (4)
$$

The transition free energy (ΔG_{ro}) of rotmers can be shown by

$$
\Delta G_{\mathrm{ro}} = {}^{\mathrm{tail}}G - {}^{\mathrm{train}}G
$$

In this system, ΔH_{ro} and ΔS_{ro} of rotmers can be related to ΔG_{ro} by

$$
\Delta G_{\mathrm{ro}} = \Delta H_{\mathrm{ro}} - T_{\mathrm{ro}}\Delta S_{\mathrm{ro}} \quad (5)
$$

where

$$
\Delta H_{\mathrm{ro}} = {}^{\mathrm{tail}}E_{\mathrm{rot}} - {}^{\mathrm{train}}E_{\mathrm{rotmer-surf}}
$$

$$
\Delta S_{\mathrm{ro}} = {}^{\mathrm{tail}}S - {}^{\mathrm{train}}S \quad (6)
$$

Assuming that the rotmers form an isolated single polymer chain and satisfy requirements i to vii, populations of rotmers in the tail state and the train state can be used as the values of F_{tail} and F_{train} obtained by the simulation of the peroxide ends of the isolated single polymer chains. Assuming that the populations of rotmers at the train state and at the tail state can be exhibited by the Boltzmann distribution function, the ratio of the population of rotmers at the tail state to that at the train state can be expressed by

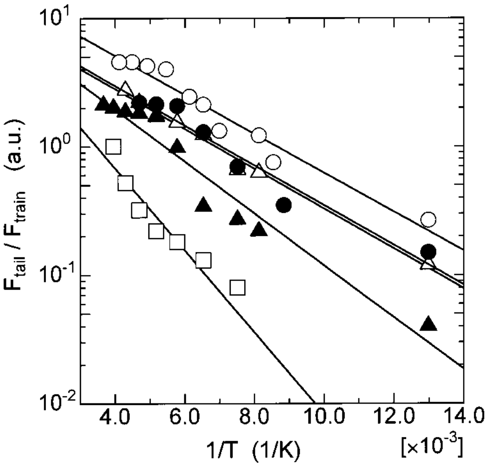

Figure 4. $\ln(F_{\mathrm{tail}}/F_{\mathrm{train}})$ plots against $1/T$ for PTFE−PE−O_2 (open circles), PTFE−PBD−O_2 (solid circles), PTFE−PP−O_2 (open triangles), PTFE−PIB−O_2 (solid triangles), and PTFE−PMMA−O_2 (squares). Each line is drawn by a least-squares fit.

$$
F_{\mathrm{tail}}/F_{\mathrm{train}} = \exp(-\Delta G_{\mathrm{ro}}/\kappa N_{\mathrm{A}}T) = \exp(-(\Delta H_{\mathrm{ro}} - T\Delta S_{\mathrm{ro}})/\kappa N_{\mathrm{A}}T) \quad (7)
$$

where κ, N_{A}, and T are the Boltzmann constant, Avogadro's number, and the observation temperature, respectively.

Figure 4 shows the plots of F_{tail} to the inverse observation temperature. ΔH_{ro} and ΔS_{ro} for each sample were estimated from the slopes of the least-squares fitted lines and the extrapolated values of $\ln(F_{\mathrm{tail}}/F_{\mathrm{train}})$ at $T = 0$ of the lines in Figure 4. These values are listed in Table 1.

The guidelines in Figure 3, which were shown by the function of the $\ln(F_{\mathrm{tail}}/F_{\mathrm{train}})$ with T, were drawn by eq 7 using the obtained values of the ΔH_{ro} and ΔS_{ro}.

Figure 5 shows the plots of ΔS_{ro} against T_{ro} (open circles). ΔS_{ro} is constant in relation to T_{ro}. The plots of ΔS_{ro} against M_{ro} (solid circles) show that ΔS_{ro} is constant in relation to M_{ro}. These results provide evidence for the assumptions in the previous paper[11] that the transition entropy is independent of both the transition temperature and the size of a conformer which is related to M_{ro} in our case.

At T_{ro}, the freely rotating rotmers and the frozen rotmers are equal in population due to the definition of T_{ro}. Thus, the ratio of the population at T_{ro} can be shown with the unity of $F_{\mathrm{tail}}/F_{\mathrm{train}}$ by

$$
F_{\mathrm{tail}}/F_{\mathrm{train}} = 1 = \exp(-(\Delta H_{\mathrm{ro}} - T_{\mathrm{ro}}\Delta S_{\mathrm{ro}})/\kappa N_{\mathrm{A}}T_{\mathrm{ro}})
$$

Then

$$
\Delta H_{\mathrm{ro}} = T_{\mathrm{ro}}\Delta S_{\mathrm{ro}} \quad (8)
$$

Since ΔS_{ro} is constant in relation to T_{ro} (Figure 5), eq 8 can be shown by

$$
\Delta H_{\mathrm{ro}} \propto T_{\mathrm{ro}} \quad (9)
$$

Consequently, it can be predicted that ΔH_{ro} will appear

Table 1. Characterization of Rotmers with Peroxide Ends and Their Thermodynamic Parameters

polymer (rotmer) (g/mol)	M_m	N_r	M_{ro} (g/mol) = $(M_m + M_{oo})/(N_r + 1)^a$	ΔH_{ro} (kJ/mol)	ΔS_{ro} (J/mol.K)	$T_{ro}{}^b$ (K)
PTFE−PE−O_2	28	2	20.0	3.06 ± 0.07	25.8 ± 0.6	123
PTFE−PBD−O_2	54	3	21.5	2.97 ± 0.08	20.9 ± 0.6	142
PTFE−PP−O_2	42	2	24.7	2.97 ± 0.02	20.5 ± 0.1	145
PTFE−PIB−O_2	56	2	29.3	3.9 ± 0.1	21.0 ± 0.6	174
PTFE−PMMA−O_2	100	2	44.0	6.1 ± 0.3	21 ± 1	253

[a] M_{oo} = 32 g/mol. [b] The errors of T_{ro} are estimated to be ±2 K.

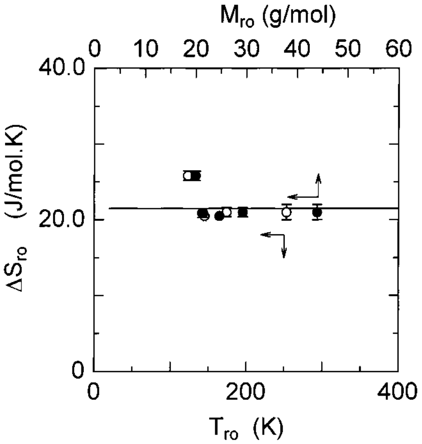

Figure 5. The plots of T_{ro} vs ΔS_{ro} and M_{ro} vs ΔS_{ro} are shown with open circles and solid circles, respectively.

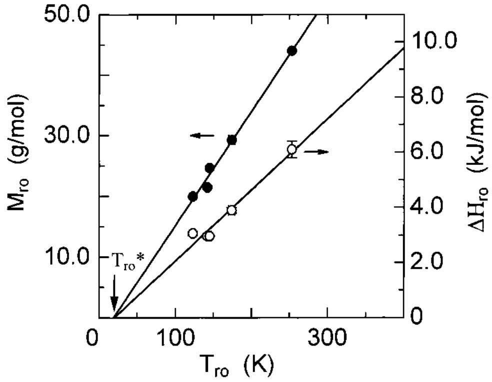

Figure 6. The plots of T_{ro} vs ΔH_{ro} and T_{ro} vs M_{ro} are shown with open circles and solid circles, respectively. The straight lines are drawn by least-squares fits. T^*_{ro}, 20 K, is a critical transition temperature.

as a linear function of T_{ro}. The prediction is evidenced in Figure 6 with open circles. ΔH_{ro} increases with an increase in T_{ro}.

$$\Delta H_{ro} = -0.5 + 0.0257T_{ro} \tag{10}$$

Equation 10 was obtained by a least-squares fit of ΔH_{ro} vs T_{ro} plots in Figure 6 with open circles. In this system, ΔH_{ro} must be satisfied;

$$\Delta H_{ro} = {}^{tail}E_{rot} - {}^{train}E_{rotmer-surf} \geq 0 \tag{11}$$

In other words, the train−tail transition can occur under the condition; ${}^{tail}E_{rot} \geq {}^{train}E_{rotmer-surf}$, i.e., the condition, in which the rotmer has enough energy to leave the PTFE surface. The critical transition temperature (T_{ro}* = 20 K) was deduced from eq 10. If T_{ro} is lower than T_{ro}*, the train−tail transition does not occur, and the rotmers are adsorbed on the PTFE surface because ${}^{tail}E_{rot} < {}^{train}E_{rotmer-surf}$. Thus, eqs 8 and 10 are only available in the temperature region

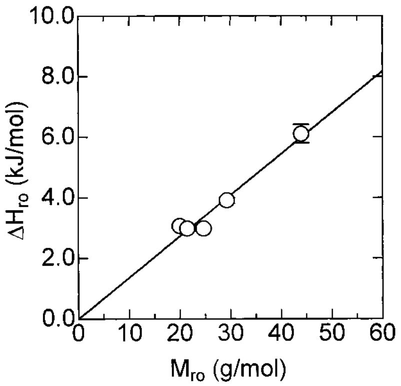

Figure 7. ΔH_{ro} dependency on M_{ro}. The straight line is drawn by a least-squares fit.

$$T_{ro} \geq T_{ro}{}^* \tag{12}$$

Generally, ${}^{tail}E_{rot}$ of the rotmer with M_{ro} can be shown by

$${}^{tail}E_{rot} = 1/2(M_{ro} \times 10^{-3})r^2\omega^2 \tag{13}$$

where ω and r are the angular velocity and distance from the center of the rotation, respectively. ω and r are still not evaluated. However, if it is assumed that $r^2\omega^2$ is constant at the train−tail transition, eq 13 can be shown by

$${}^{tail}E_{rot} \propto M_{ro}$$

And assuming for simplicity

$${}^{tail}E_{rotmer-surf} \propto M_{ro}$$

then, eq 6 can be expressed by

$$\Delta H_{ro} \propto M_{ro} \tag{14}$$

Thus, ΔH_{ro} can be shown as a linear function of M_{ro}. Evidence for this prediction is shown in Figure 7, in which ΔH_{ro} plots against M_{ro}. ΔH_{ro} increases with an increase in M_{ro}.

$$\Delta H_{ro} = 0.136M_{ro} \tag{15}$$

which was obtained by a least-squares fit of ΔH_{ro} vs M_{ro} plots in Figure 7.

From eqs 9 and 14, the relationship between T_{ro} and M_{ro} can be deduced to be

$$T_{ro} \propto M_{ro} \tag{16}$$

Evidence for this is given in Figure 6 with solid circles. T_{ro} increases with an increase in M_{ro}.

$$T_{ro} = 20 + 5.26M_{ro} \quad (17)$$

which was obtained by a least-squares fit of T_{ro} vs M_{ro} plots in Figure 6.

The thermodynamic values, ΔH_{ro}, and ΔS_{ro} were estimated, and the linear relationships among ΔH_{ro}, ΔS_{ro}, T_{ro}, and M_{ro} were obtained because the rotmers which form isolated single polymer chains tethered to the PTFE surface in vacuo satisfy the requirements from (i) to (vii), i.e., the isolated rotmers.

References and Notes

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