Molecular Motion of Chain End Peroxy Radicals of Polyethylene Molecules Tethered on a Fresh Surface of Poly(tetrafluoroethylene)

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ABSTRACT: Chain end peroxy radicals of polyethylene (PE) molecules tethered on a fresh surface of poly(tetrafluoroethylene) (PTFE) were produced in the following way. Ethylene monomer was block copolymerized by initiation of mechanoradicals formed by mechanical fracture of the PTFE powder. The propagating radical in the block copolymerization, $-CH_2CH_2^•$, located on the fresh surface of PTFE was converted into peroxy radicals, $-CH_2CH_2OO^•$, after introduction of oxygen molecules. Temperature−dependent ESR spectra of the peroxy radicals were successfully observed. The remarkable change with anisotropic *g*-values of the radicals was analyzed by computer simulation, and it was found that the PE peroxy radicals on the PTFE surface have extremely high mobility in comparison with the PE radicals on the PE surface and the PTFE radicals on the PTFE surface. This is a reflection of the properties of the protruding PE chains on the PTFE surface; i.e., interaction between PE chains from the PTFE surface must be much weaker than those on the surface of the homopolymer, because of the extremely low segmental concentration of the PE molecules on the PTFE surface.

Introduction

In our previous paper,[1] ESR spectra of PE alkyl radicals, $-CH_2CH_2^•$, were interpreted in terms of a spin exchange of protons between equilibrium states occurring at dihedral angles of 15 and 45°, and it was concluded that the molecular motion of the chain end radical of a PE molecule tethered on a PTFE surface has a high mobility, even at temperatures as low as 77 K. In this article, a similarly high mobility of peroxy radicals will be described. The peroxy radicals are much more stable than the alkyl radicals. The molecular mobility of the chains in the higher temperature region could be elucidated from the temperature-dependent ESR spectra of the peroxy radicals. The ESR spectra of the peroxy radicals of polyethylene[2−5] and poly(tetrafluoroethylene)[6−10] have been studied by many authors. Hori et al.[3] found that the observed ESR spectra are composed of two spectra arising from chemically identical peroxy radicals, having different mobilities and stabilities, and carried out computer simulation of those spectra to determine the anisotropic *g*-values as well as the ratio of the amounts of the radicals located at the respective radical sites. We can elucidate the structure and dynamic behavior of PE chains at a particular region of the PTFE surface from a detailed analysis of the changes of the anisotropic *g*-values with temperature. In this paper, we compare the mobility of PE peroxy radicals on the PTFE surface with those of PE radicals on the PE surface and PTFE radicals on the PTFE surface and clarify the molecular motion of the chains tethered on the polymer surfaces, related to the structure of the chains.

Experimental Section

Materials. Polyethylene (PE) (Sholex 6050, Showa Electric Industry Co., Ltd.) was used after the purification mentioned in our previous paper.[1] Poly(tetrafluoroethylene) (PTFE) (Aflon G-80, Asahi Glass Co., Ltd.) was used without purification. Ethylene monomer (Takatiho Co., Ltd.) was purified by the freeze−pump−thaw method.

Mechanical Fracture. Mechanical fracture of the polymer with or without ethylene monomer was carried out by milling in a homemade vibration glass ball mill in vacuo at 77 K.[11] After the milling, the ESR sample tube connected to the glass ball mill was placed in liquid nitrogen, and the powdered sample was dropped into the ESR sample tube within 1 s by turning the glass ball mill upside down. After the alkyl radicals at the chain end were observed, oxygen molecules at a pressure of 160 Torr were introduced into the ampule, and the polymer chains on the surface were labeled with peroxy radicals.

(A) The PTFE sample with ethylene monomer was milled for 8 h and the polyethylene molecules tethered on the PTFE surface were produced by block copolymerization of ethylene monomer, which was initiated by mechanoradicals. Subsequently, oxygen was introduced to the sample at 77 K. This was coded as the PTFE/C_2H_4/O_2 specimen.

(B) The PTFE sample without ethylene monomer was milled for 8 h and the chain end radical of PTFE was trapped on the PTFE surface. Subsequently, oxygen was introduced to the sample at 77 K. This was coded as the PTFE/O_2 specimen.

In both PTFE/C_2H_4/O_2 and PTFE/O_2, all of the alkyl radicals were converted to peroxy radicals during annealing at 158 K for 30 min, as described in the next section.

(C) The PE sample without ethylene monomer was milled for 24 h. Almost all chain end radicals of PE were trapped on the PE surface. Subsequently, oxygen was introduced to the sample at 77 K. This was coded as the PE/O_2 specimen. All of the alkyl radicals were converted to peroxy radicals during annealing at 203 K for 30 min.

ESR Measurements. ESR spectra at 4 K, 77 K, and higher temperatures 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 diphenylpicrylhydrazyl (DPPH) was used as a *g*-value standard. The magnetic field sweep was calibrated with known splitting constants of Mn^{2+}.

Spectral Simulation. The computer simulation developed by Hori et al.[3] 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

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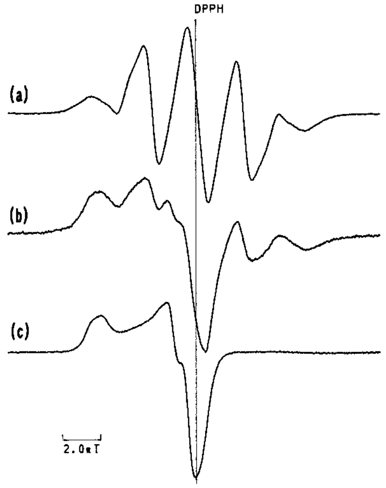

Figure 1. ESR spectra of PE chain end radicals before (a) and after (b,c) introduction of oxygen molecules at 77 K [(b) storage at 77 K for 30 min; (c) annealing at 158 K for 30 min]. Measurements were carried out at 77 K.

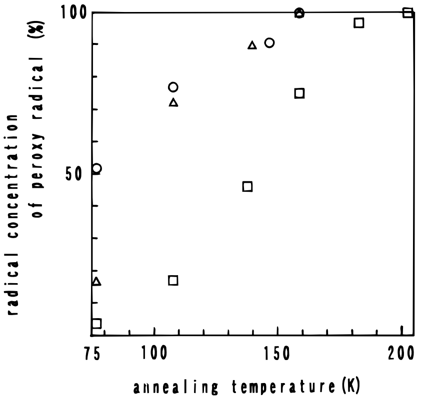

Figure 2. Change in peroxy radical concentration with annealing temperature: (○) PTFE/C_2H_4/O_2; (△) PTFE/O_2; (□) PE/O_2;

mobile and rigid 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

Oxidation of Chain End Alkyl Radicals on the Polymer Surface. The peroxy radicals were produced by reaction of the chain end alkyl radicals with oxygen. Figure 1 shows changes of the ESR spectra of the PE alkyl radicals on the PTFE surface (PTFE/C_2H_4/O_2) with the reaction of oxygen. More than 50% of the alkyl radicals were converted into peroxy radicals even at 77 K for 30 min, and we were successful in converting all of the alkyl radicals to peroxy radicals during annealing at 158 K for 30 min. In Figure 2, the "growing curves" of peroxy radicals are shown for the PTFE/C_2H_4/O_2, PTFE/O_2, and PE/O_2 specimens. After introduction of oxygen molecules at 77 K, each sample was annealed at a desired temperature for 30 min and subsequently plunged into liquid nitrogen. The ESR measurements were carried out at 77 K.

The growing curves were obtained by repeating these procedures with increasing annealing temperature. The growing curves of the respective specimens were different. For example, the peroxy radicals in the PE/O_2 specimen begin to grow at a higher annealing temperature, 108 K, than those in the other specimens. The growing rate of the peroxy radicals at 77 K in the PTFE/C_2H_4/O_2 specimen is the largest of three samples.

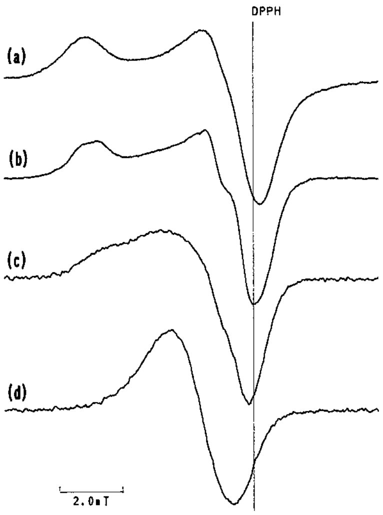

Figure 3. ESR spectra of PE peroxy radicals on a PTFE surface (PTFE/C_2H_4/O_2) obtained at various temperatures: (a) 4 K; (b) 77 K; (c) 123 K; (d) 183 K. The vertical line indicates the position of the spectrum of DPPH, $g = 2.0036$.

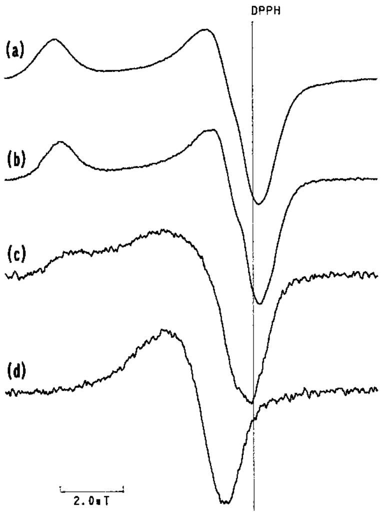

Figure 4. ESR spectra of PTFE peroxy radicals on a PTFE surface (PTFE/O_2) obtained at various temperatures: (a) 4 K; (b) 77 K; (c) 163 K; (d) 223 K. The vertical line indicates the position of the spectrum of DPPH, $g = 2.0036$.

These experimental facts are reflected on the structures of the chain end radicals on the polymer surfaces. The polyethylene chains on the PTFE surface should protrude from the surface and then have low segmental density because of immiscibility of both chains. On the other hand, almost all PE chains on the PE surface and almost all PTFE chains on the PTFE surface should be surrounded by the same homopolymer chains. Consequently, the alkyl radicals of the protruded PE chains on the PTFE surface are apt to be attacked by oxygen molecules.

Structure and Molecular Motion of Peroxy Radicals on the Polymer Surface. Figure 3 shows the temperature dependence of the ESR spectra of the PE peroxy radicals on the PTFE surface (PTFE/C_2H_4/O_2), and Figures 4 and 5 show the temperature dependencies of the ESR spectra of the PTFE (PTFE/O_2) and PE (PE/O_2) peroxy radicals on the PTFE and PE surfaces,

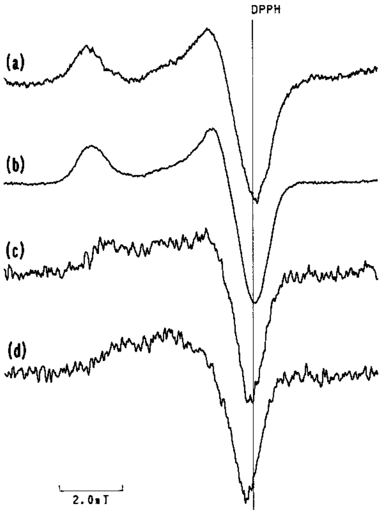

Figure 5. ESR spectra of PE peroxy radicals on a PE surface (PE/O_2) obtained at various temperatures: (a) 4 K; (b) 77 K; (c) 187 K; (d) 223 K. The vertical line indicates the position of the spectrum of DPPH, $g = 2.0036$.

Table 1. Spectroscopic Parameters (g-Values and Average Line Width, (ΔH_{av})) for the ESR Spectra of Peroxy Radicals Observed at 4 K

	g_1	g_2	g_3	ΔH_{av} (mT)
$PTFE/C_2H_4/O_2$	2.0019	2.0079	2.0368	1.85
$PTFE/O_2$	2.0018	2.0081	2.0429	1.17
PE/O_2	2.0022	2.0081	2.0365	0.88

respectively. The following characteristics of the ESR spectra for the $PTFE/C_2H_4/O_2$ specimen were found in comparison with the other cases ($PTFE/O_2$, PE/O_2).

(a) High Molecular Mobility at 77 K. The spectrum observed at 77 K is different from that at 4 K. (Figure 2a,b) Small humps inside the g_1 and g_3 peaks are observed in the spectrum at 77 K. This fact suggests that some PE peroxy radicals on the PTFE surface have already begun to move at 77 K.

(b) Peculiar Trapped Structure at 4 K. It was confirmed that the molecular motion of the polymer chains tethered on the polymer surfaces was in a frozen state at 4 K. The observed ESR spectra at 4 K from chemically identical PE peroxy radicals were compared with each other (Figures 3a and 5a). The ESR spectra were analyzed in terms of only one component by the computer simulation. The anisotropic g-values and line width determined by the simulation are shown in Table 1. The larger g_3 values for the PTFE peroxy radicals should be attributed to the effect of the fluorine atoms, as is well known.[7] The line width (1.9 mT) of the spectrum of the peroxy radicals on the PTFE surface is much larger than that (0.9 mT) on the PE surface in spite of both peroxy radicals having similar g-values. In general, the line width of the ESR spectrum is a function of spin−lattice (T_1) and spin−spin (T_2) relaxation times, which are affected by surrounding structures. In the present case, the wide line width of the spectrum should be caused by a broad distribution of the magnitude of the interaction between the PE peroxy radical and the fluorine nucleus on the PTFE, which has larger magnetic dipoles than the hydrogen nucleus. The PE chains should begin to protrude from the PTFE surface with increasing temperature, because of the increasing repulsion between the PE and PTFE chains.

(c) High Molecular Mobility at Higher Temperatures, Related to the Protruding Structure. (1) Molecular Mobility. The computer simulation was

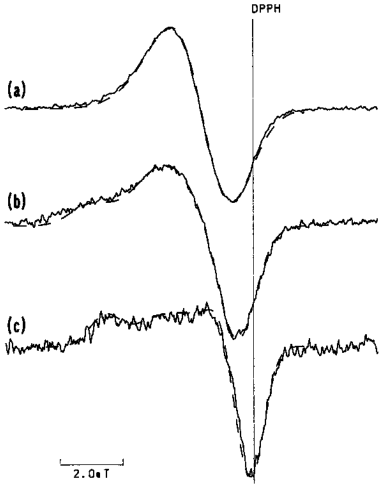

Figure 6. Examples of spectrum simulation [(− − −) simulation; (—) observed at 183 K]: (a) $PTFE/C_2H_4/O_2$; (b) $PTFE/O_2$; (c) PE/O_2.

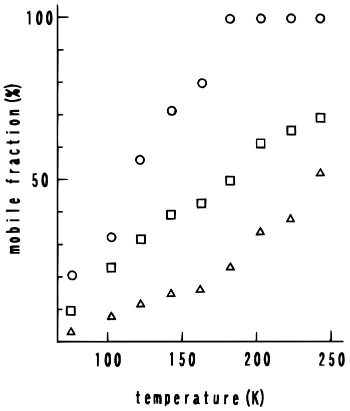

Figure 7. Changes in mobile fraction with temperature: (○) $PTFE/C_2H_4/O_2$; (□) $PTFE/O_2$; (△) PE/O_2.

carried out to obtain several parameters and to confirm the coexistence of two kinds of radicals, having different mobilities. Figure 6 shows examples of the best fit spectra and the experimental spectra observed at 183 K. The agreement between the simulated spectra and the observed spectra is excellent and indicates the classification of the radicals into A- and B-radicals was a good approximation. From the simulation in Figure 6, the fractional amounts of the mobile radicals at 183 K were estimated to be 100, 50, and 23% for the $PTFE/C_2H_4/O_2$, $PTFE/O_2$, and PE/O_2 specimens, respectively. Hori et al.[4] interpreted the temperature dependence of the fractional amount in terms of a distribution of correlation times of A- and B-radical sites. Cameron et al.[12] also interpreted the double-peak feature of the ESR spectrum of a nitroxide spin probe as reflecting tumbling with a distribution of correlation times arising from a distribution of free volume within a polymer matrix. Heterogeneous structures of the chains on the polymer surface should be responsible for a broad distribution of correlation times.

Because of the lower shift of the average correlation time with increasing temperature, the fractional amount of the mobile radicals should increase with temperature. Figure 7 shows the change of the fractional amount with temperature obtained from the spectral simulation. The mobile fraction for the $PTFE/C_2H_4/O_2$ specimen begins to increase in the lowest temperature region, whereas slow changes with temperature are observed for the other specimens. The mobile fraction for the PE/O_2

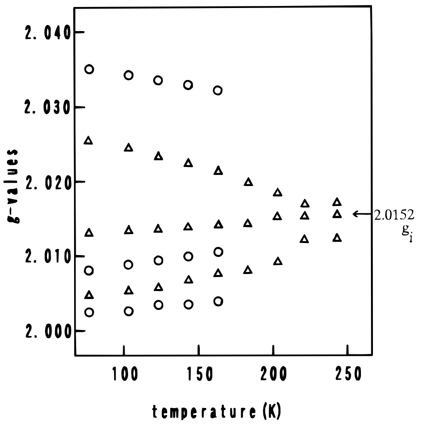

Figure 8. Change of g-values with temperature (PTFE/C_2H_4/O_2): (○) A-radical (rigid radical); (△) B-radical (mobile radical).

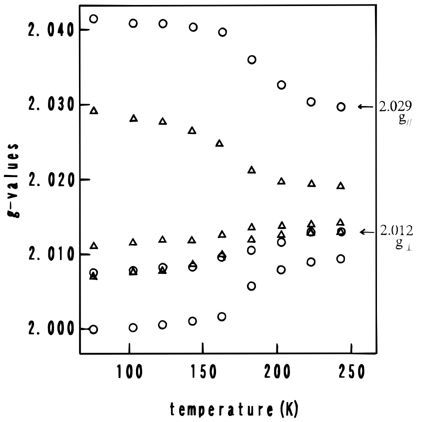

Figure 9. Change of g-value with temperature (PTFE/O_2): (○ A-radical (rigid radical); (△) B-radical (mobile radical).

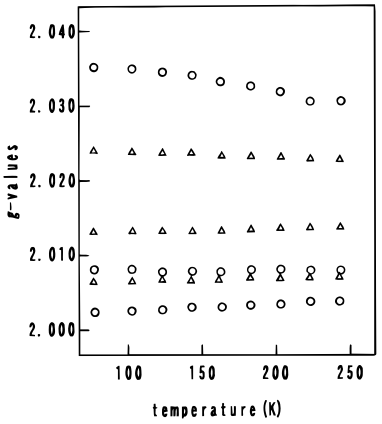

Figure 10. Change of g-value with temperature (PE/O_2): (○) A-radical (rigid radical); (△) B-radical (mobile radical).

specimen is the smallest in the temperature range examined. As seen in Figures 6 and 7, it was confirmed that the PE molecules tethered on the PTFE surface have the highest mobility. The molecular motion of the chains allows nearly free rotation at more than 163 K, where ESR spectra were analyzed in terms of only one component.

(2) Mode of Molecular Motion. Changes of the anisotropic g-values with temperature are shown in Figures 8–10 for PTFE/C_2H_4/O_2, PTFE/O_2, and PE/O_2, respectively. As seen in the figures, the largest g-value for the A-radicals (g_3) is larger than the corresponding value for the B-radical (g_3'), whereas the other g-values for the A-radicals (g_1, g_2) are smaller than the corresponding values for the B-radicals at all temperatures for all specimens. These facts indicate that the molecular motion of the B-radical sites is more rapid than that of the A-radical sites at every temperature.

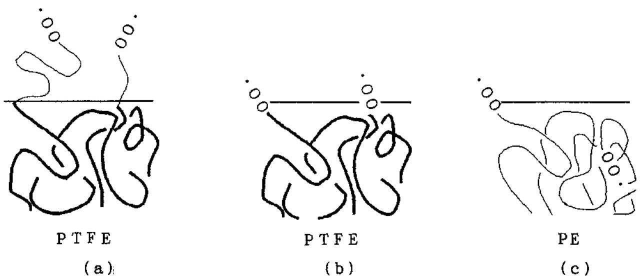

Figure 11. Schematic illustration of the location of the chain end peroxy radical of polymer chains tethered on a solid surface: (a) PE radical on a PTFE surface; (b) PTFE radical on a PTFE surface; (c) PE radical on a PE surface. The thin lines are polyethylene chains and the heavy lines are PTFE chains.

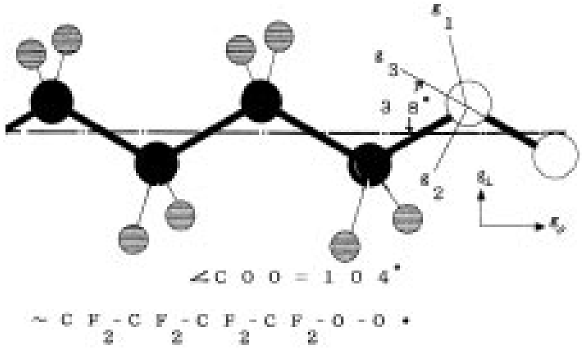

Figure 12. Conformation structure (planar zigzag structure) of the chain end peroxy radical of PTFE.

The different modes of molecular motion of the polymer chains on the surfaces of the polymers are responsible for the trapped states of the chains, as illustrated schematically in Figure 11. The motional averaging of the g-values in the PE peroxy radicals on the PTFE surface is also different from that in the PTFE radicals on the PTFE surface, as seen in Figures 8 and 9. The anisotropic g-values in the PE peroxy radicals on the PTFE surface approach the isotropic g-value, 2.0152, as shown in Figure 8. This fact indicates that the PE molecules on the PTFE surface give rise to free rotation at random in three-dimensional space. On the other hand, the motional averaging of the g-values in the PTFE peroxy A-radicals on the surface of the same polymer has a transition temperature around 163 K, and then the g-values approach the limiting values of $g_\parallel = 2.029$ and $g_\perp = 2.012$, which can be calculated on the assumption of rotation around the chain axis and the conformation of the peroxy radical[13,14] as described in Figure 12.[15]

As shown in Figure 7, the fractional amount of mobile radicals increases with temperature by the conversion of A-radicals to B-radicals. The conversion may originate from the change of the motional mode from rotation around the chain axis to free rotation and/or the addition of rapid molecular motion of the same mode. The motional averaging of the g-values should be related to more than two kinds of trapped structure of peroxy radicals on the PTFE surface, as illustrated schematically in Figure 11b.

The PE chains on the PTFE surface should protrude from the surface and then have low segmental density. On the other hand, the PTFE chains on the PTFE surface should be surrounded by the homopolymer chains. Some PTFE chains have a relatively ordered structure as if the chains are in a crystalline region. Then, the PTFE chains should restrict the molecular motion of the chain end peroxy radicals and/or give rise to the axially symmetrical rotation or vibration around the chain axis. The anisotropic g-values of the PE peroxy radicals on the PE surface (PE/O_2) do not change with temperature, as shown in Figure 10. The temperature dependence of the ESR spectra of the radicals seems to mainly come from the change of the mobile fraction. As mentioned above, molecular motion of polymer chains on a fresh polymer surface should be strongly related to the structure of the chains. The high mobility of the PE chains on the PTFE surface is attributed to weak intermolecular forces between the PE and PTFE chains and cause the PE chains to protrude from the PTFE surface, as illustrated schematically in Figure 11a. Thus, the high mobility of the chain end peroxy radical results in specific isolation from the PTFE surface; i.e., there is a large specific volume around the radical. On the other hand, the PE and PTFE chains on the surfaces of PE and PTFE, respectively, are surrounded by the homopolymer chains, which restrict the molecular motion of the peroxy radicals.

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(15) $g_{\parallel} = g_2 \cos^2 52° + g_3 \cos^2 38° = 2.029$, $g_{\perp} = (g_1 + g_2 + g_3 - g_{\parallel})/2 = 2.012$. The values of g_1, g_2, and g_3 are experimental ones at 4 K.

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