Distribution of the grafted PS in crosslinked PTFE-*g*-PS film and the surface enrichment of the PTFE chains

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Radiation-induced graft copolymerization of styrene to the cross-linked PTFE film was carried out. FT-IR and ESCA measurements revealed the aggregation structure of the grafted polystyrene (PS). The molar ratio of PS to PTFE at the surface was higher than that of the bulk for the sample grafted at 333 K. The molar ratio at the surface decreased with raising the grafting temperature and, finally, it was smaller than that of the bulk. The surface enrichment of PTFE chains was observed. These facts were responsible for the diffusion of styrene to interior of the film, and the high mobility of PTFE chains in the amorphous region at high temperatures, and low surface free energy of PTFE. Moreover, the annealing of the film in vacuum at slightly lower temperature than T_g of PS homopolymer bulk made the enrichment of PTFE chains at the film surface. In addition, ESR measurement revealed the grafted PS had higher mobility than bulk PS.
Key words: cross-linked PTFE / polystyrene / surface enrichment / surface free energy / ESCA

1. INTRODUCTION

Polytetrafluoroethylene (PTFE) is well known to be a unique polymer, which is a heat resistant, high electrical insulation, and high stability to any chemical solvent. However, PTFE is a typical polymer to degrade during radiation.[1,2] Recently, development of the crosslinked PTFE improved the radiation resistance.[3] Therefore, the facile chemical modification (grafting) of the PTFE by radiation and high grafting degree have been expected. One of our interests of this study was a graft polymerization of styrene to the crosslinked PTFE with high grafting degree. Another interest of ours was the surface composition of the PTFE-*g*-PS film and the surface mobility.

Much attention has been focus on a structure and molecular mobility of surface of polymeric materials. It has been reported that the structure and mobility of the surface are different from those of the bulk and the mobility of the surface is activated.[4 - 8] It is of much interest and importance to study the surface properties (composition and mobility) of the PTFE-*g*-PS film. Electron spectroscopy for chemical analysis (ESCA) has been powerful method and used widely to investigate a surface composition [9,10] of polymer and, in addition, a temperature dependence of chemical composition of PMMA-*b*-PS and its molecular mobility were studied by ESCA measurement.[11]

In this paper, distribution of the grafted PS in crosslinked PTFE-*g*-PS film during graft polymerization is reported. We also characterize the surface enrichment of the PTFE chains and the mobility of the grafted PS by ESCA and electron spin resonance (ESR) techniques.

2. EXPERIMENT

2.1 Materials.

A cross-linked PTFE film (XF-2 c.a. 500 μm in thickness) was obtained from Hitachi Cable Inc. The PTFE film was washed with acetone and dried in vacuum. Styrene (ST) monomer (Nacalai Tesque, Inc.) was distilled under a reduced pressure through CaH_2. 2,2,6,6-Tetramethyl-piperidine-1-oxyl (TEMPO) as spin probe reagent was purchased from Aldrich and used without further purification. Tetrahydrofuran and methanol were purchased from Nacalai and used as received.

2.2 Graft Copolymerization.

Some cross-linked PTFE (5 mm x 30 mm) films were irradiated with ^{60}Co γ-ray at a rate of 156 Gy/h in air. Total dose was 34.5 kGy. The oxidized PTFE films were immersed in ST monomer in a glass tube. The glass tube was degassed by three times freeze-and thaw method and sealed in vacuum. The glass tube was heated to 333-398 K to conduct a graft polymerization of styrene to the PTFE films. After the polymerization, the PTFE film grafted with PS was washed by Soxhlet apparatus with toluene and the free PS (non-grafted PS) was extracted. The PS grafted to PTFE (PS-*g*-PTFE) films were dried at 60°C for 24h and room temperature for at least 48h in vacuum. A grafting ratio *GR* (mol%) was defined to be molar ratio of PS (repeat unit) to PTFE (repeat unit).

2.3 ESCA measurement.

Electron spectroscopy for chemical analysis (ESCA) data were obtained using X-probe SSX-100 (JSSI Inc.) spectrometer employing exciting radiation of 1487 eV (Al*K*α) and energy neutralization gun. All spectra were referenced to the C_{1s} peak for PS carbon, which was assigned a value of 285 eV, and were recorded at an electron take-off angle of 30-90° with respect to the polymer surface.

2.4 Spin probe and ESR measurement.

The PS-*g*-PTFE film was immersed in THF solution containing TEMPO at room temperature for 24h in order to dope it in the film. The spin-probed films were washed by Soxhlet with methanol and dried in vacuum for 48h. ESR spectra of the probed PS-*g*-PTFE samples were observed in vacuo at a lower microwave power level to avoid power saturation and with 100 kHz field modulation using JEOL JES-FE3XG at 77K and JES-RE1XG spectrometers above 113K. The signal of 1,1-diphenyl-2-picrylhydrazyl was used as a *g*-value standard. The magnetic field calibrated with the well-known splitting constants of Mn^{2+} in MgO.

2.5 FT-IR measurement.

FT-IR spectra were observed using IMPACT 400D (Nicolet Instruments Co.). The accumulation was 64 times.

3. RESULT AND DISCUSSION

3.1 Distribution of the grafted PS and the surface composition.

The graft polymerizations were conducted at various temperatures in this study and the *GR* is widely known to depend on the temperature. And it is expected that polymerization temperature affect a distribution of the grafted PS in the film. These seem due to the stability of the peroxides as initiators of grafting.

To observe the region of grafted PS in the PTFE-*g*-PS film, the films was sliced in every 20 μm in thickness by a microtome and then FT-IR spectra of them was measured. Peak intensities of 720 and 698 cm⁻¹ were used as a measure of the *GR*, which are assigned to C-F stretching vibration in $CF-CF_2$ group of PTFE and C-H bending vibration of benzene ring. Figure 1 shows the intensity ratios A_{698}/A_{720} of the PTFE-*g*-PS samples (solid) and (open) prepared at 333 and 398 K for 2h, respectively. Although both samples had almost the same *GR* of ~14 mol%, the distributions were quite different. The grafted PS was distributed in more interior region with an increase in grafting temperature (333-398 K). These are caused by higher probability of a diffusion of styrene monomer to the interior since the mobility of PTFE chains was much activated at higher temperature. In the case of the graft copolymerization at 333 K, the maximum of the absorbance ratio around 80μm in depth was observed. This seems to relate with the grafting rate constant, the diffusion of the styrene, and stability of the peroxide. That is, ST monomer concentration decreases toward into the film center, the grafting rate constant becomes low when monomer concentration in the film increases [12], and the peroxide near the surface is probably most unstable. These reasons may be responsible for appearance of the maximum of *GR* in the film.

Table I shows the bulk (GR_B) and surface *GR* (GR_S) that were determined by gravimetric method and ESCA measurement, respectively. Both *GR* were different, i.e., the surface composition was significantly different from the bulk one. As a measure of the surface enrichment of PTFE chains, GR_S/GR_B was determined for each sample. When the GR_S/GR_B is smaller than unity, the PTFE chains are enriched at the surface. In the case of short polymerization time or low polymerization temperature,
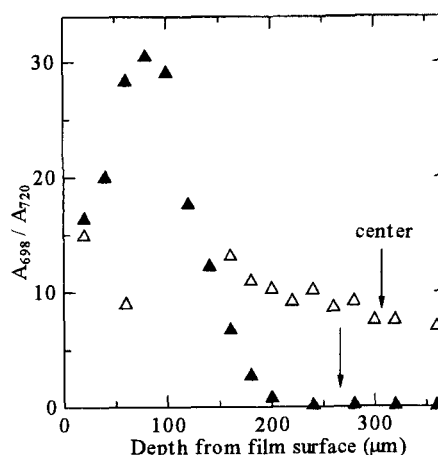

Figure 1. Concentration profiles of polystyrene in the PTFE-*g*-PS polymerized at 333 (solid) and 398 K (open) for 2h. Centers of the film were marked with arrows.

Table I. Bulk and Surface Grafting Ratio

Temp.[a]	Time[a]	GR_B[b]	GR_S[c]	GR_S/GR_B
333	1.5	6.9	17.0	2.46
333	5	22.1	78.3	3.54
333	10	73.3	31.6	0.43
373	1	11.6	62.4	5.38
373	5	30.2	27.7	0.92
398	1	6.5	16.1	2.48
398	2	19.3	4.2	0.22
398	8	32.5	9.5	0.29

[a] polymerization temperature (K) and time (h), [b] bulk *GR* (mol%) determined by gravimetric method, [c] surface *GR* (mol%) determined by C_{1s} core-level spectra at an electron take-off angle of 30°

the trend that the surface *GR* was much higher than bulk *GR* was observed. In other words, the PTFE fraction at the surface increased with increasing polymerization time or temperature. The graft initiating point near the surface was consumed at lower temperature or for shorter time. As grafting temperature and time increases, the grafting can be limited in the interior region of the film. Therefore, the increase in GR_B was almost arising from an increase in PS fraction in the interior region of the film.

3.2 Annealing temperature dependence of the surface composition of PTFE-*g*-PS film.

Figure 2 shows the change in the molar ratio (surface *GR*) of ST to PTFE for PTFE-*g*-PS having the bulk *GR* 44 mol% with annealing temperature *in vacuo*. The inset shows the C_{1s} core-level spectrum of PTFE-*g*-PS at the electron take-off angle of 30°, hence, the information was from about 30Å in depth. The peaks of 285 and 292 eV were assigned to PS and PTFE carbons, respectively. The peak of 292 eV include the π-π* shake-up peak from a benzene ring in polystyrene. The peak intensity of π-π* shake-up is 10 – 20 times as small as that of the main peak (285 eV) for PS. Taking this point into account, the surface *GR* was calculated from the area ratio of C-H to C-F peaks. After the polymerization (without annealing), the surface *GR* was considerably
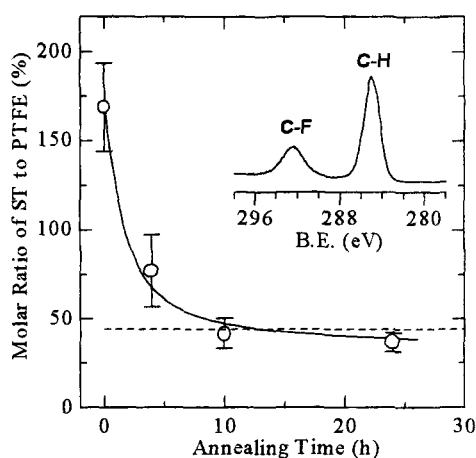
Figure 2. Change in the ratio of ST to PTFE on annealing time at 393 K *in vacuo*. Graft polymerization was carried out at 333 K. Bulk *GR* was 44 mol% drawn with broken line. Inset was C_{1s} core-level spectrum of the PTFE-*g*-PS at the electron take-off angle of 30°.

higher than the bulk *GR*, i.e. the grafted PS was located near the surface (depth of 30Å). Annealing at 393 K above T_g of PS bulk dramatically changed the surface composition. The surface *GR* reached the bulk *GR* after annealing for 10h. The limit value seems to be lower than the surface *GR*. This composition change was responsible for the difference of surface free energy between PS (40.7 mJ/m²) and PTFE (20 mJ/m²). At 393 K, PS and amorphous PTFE chains are mobile and PTFE chains moved to the surface region to reduce the surface free energy of the PTFE-*g*-PS film. That is, the *surface enrichment of the PTFE chains was observed by annealing in vacuo*. The surface enrichment is associated with the molecular motion of the PS and PTFE chains at the surface, i.e. the surface mobility of the chains.

The composition change of its surface on annealing temperature was investigated by ESCA. Figure 3 shows the surface compositions plotted against annealing temperature. Each sample had the same bulk *GR* of 44 mol% and the annealing time was 24 h. The fraction of PS (*GR*) decreased steeply around 358 K. The T_g of PS bulk is often referred to be about 373 K. The surface composition change occurred at below the T_g of PS. It is noteworthy that time scale should be important factor. In general, the relaxation time $\tau(T_g)$ at T_g was 100 s [13] The observation time scale is much smaller than 24 h in our present study. The transition temperature, T of PS bulk for the time scale $\tau(T)$ is calculated by using WLF equation.

$$\log \frac{\tau(T)}{\tau(T_g)} = \frac{-C_1(T-T_g)}{C_2+T-T_g}$$

Here, C_1 and C_2 are WLF parameters for PS taken from the literature to be 13.7 and 50.0 K, respectively.[14] When $\tau(T)$ is 8.6×10^4 s (24 h) and $\tau(T_g)$ for PS bulk is 100 s, the transition temperature T of PS bulk (homopolymer) is calculated to be about 364 K at $\tau(T) = 8.6 \times 10^4$ s. This temperature is close to the temperature of the composition change of the film surface. Log[$\tau(T)/\tau(T_g)$] is overestimated in this time scale range using WLF equation, and then the calculated transition
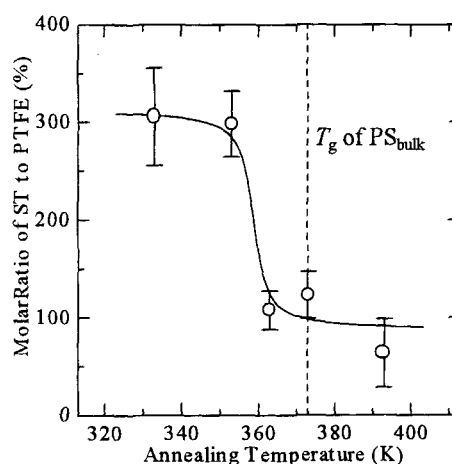

Figure 3. Annealing temperature dependence of molar ratio of PS to PTFE, which was analyzed by ESCA measurement. Each sample was annealed for 24h. T_g of PS bulk was drawn with dashed line.

temperature is about 4 K lower than true one. The glass transition temperature at $\tau(T)$ of 8.6×10^4 s is expected to be about 368 K. In addition, for the surface enrichment of PTFE chains in this system, the larger scale of the molecular motion of the grafted PS than the micro Brownian motion must occur. The change of the surface composition around 358 K suggested that the transition temperature of the graft PS near the surface should be much lower than 358 K. Therefore, the mobility of PS near the surface detected by ESCA was concluded to be higher than bulk PS (homopolymer).

3.3 Molecular mobility of grafted PS detected by ESR

In order to confirm whether the T_g of PTFE-*g*-PS is lower than that of PS bulk, the molecular mobility of the grafted PS is studied by ESR spin probe technique. To check if TEMPO molecules were probed in only PS chain, both γ-irradiated PTFE and PTFE-*g*-PS samples were probed by the same procedure.
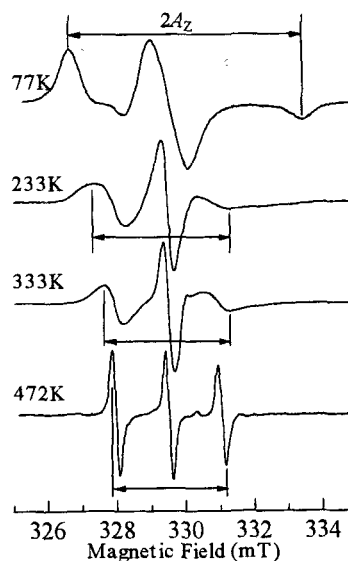

Figure 4. ESR spectra of PTFE-g-PS (*GR* = 7.8mol%) observed at various temperatures
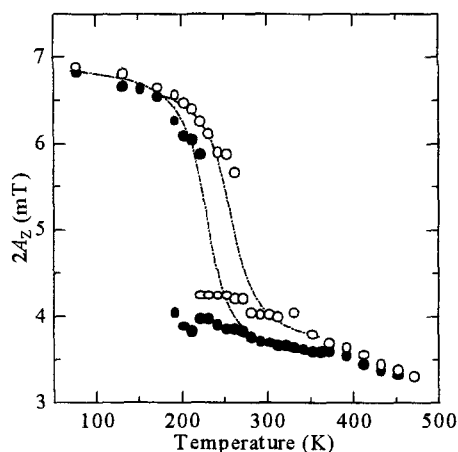
Figure 5. Temperature dependence of outermost splitting $2A_z$ for PTFE-g-PS (solid) having GR of 7.8 mol% and PS homopolymer bulk (open).

No ESR signal of TEMPO was observed in the γ-irradiated PTFE sample but in the PTFE-g-PS samples. Thus, TEMPO molecules were located in the grafted PS. The temperature dependent ESR spectra indicated the mobility of the grafted PS. Figure 4 shows the spectra for the PTFE-g-PS film having bulk GR of 7.8 mol% at various temperatures. In general, the outermost splitting width $2A_z$ of the main triplet spectrum due to hyperfine coupling constant caused by the nitrogen nucleus narrows with an increase in mobility of the radicals because of motional averaging of the anisotropic interaction between electron and nucleus. The complete averaging gives rise to the isotropic narrowed spectrum. The outer most splitting $2A_z$ between lines indicated in Figure 4 gradually narrows with an increase in temperature.

Temperature dependences of the $2A_z$ for the PTFE-g-PS and PS homopolymer bulk are shown in Figure 5 with solid and open circles, respectively. The transition temperature at which $2A_z$ equals to 5.0mT is defined as $T_{5.0mT}$. The $T_{5.0mT}$'s were estimated to be 229 and 259 K for PTFE-g-PS and PS bulk, respectively. The transition temperature of grafted PS was 30 K lower than that of the PS bulk. The $T_{5.0mT}$ were independent on the bulk GR. It is important to discuss the location where TEMPO molecules are probed in the PTFE-g-PS film. Angular dependent N1s core-level spectra of the film N1s peak (400 eV) from TEMPO molecules at the electron take-off angle of 30 and 90° was observed in the PTFE-g-PS film. The TEMPO molecules were present at least near the surface at c.a. 25Å. Unfortunately, the probed TEMPO over the depth of c.a. 50 Å was unable to be detected by ESCA. Though the inside of the film was not known about the location of TEMPO, it was found out that TEMPO was probed near the film surface at least, although the TEMPO molecules may be probed in the interior region of the film. The ESR measurement also revealed the grafted PS had higher mobility than bulk PS. The ESR result was closely related to the surface enrichment of PTFE chains of PTFE-g-PS film below the T_g of PS bulk.

4. CONCLUSION

Radiation-induced graft copolymerization of styrene to the cross-linked PTFE film was carried out. FT-IR and ESCA measurements revealed the aggregation structure of the grafted polystyrene (PS). The molar ratio of PS to PTFE at the surface (surface GR) was higher than that in the bulk ratio (bulk GR) in the grafting temperature of 60°C. The surface GR decreased with raising the grafting temperature and was smaller than that of the bulk. The surface enrichment of PTFE chains was observed. These facts were responsible for the diffusion of styrene to interior of the film, and the high mobility of PTFE chains in the amorphous region at high temperatures, and low surface free energy of PTFE. Moreover, the annealing of the film at slightly lower temperature than T_g of PS homopolymer bulk in vacuum move the PTFE chains to the film surface. In addition, ESR measurement revealed the grafted PS had higher mobility than bulk PS.

5 REFERENCES

[1] A. Charlseby, *Nucleonic*, 12, 18 (1954).
[2] L. A. Wall and R. E. Fluorin, *J. Appl. Polym. Sci.*, 2, 251 (1959).
[3] A. Oshima, S. Ikeda, T. Seguchi, and Y. Tabata, *Radiat. Phys. Chem.* 48, 755 (1666).
[4] T. Kajiyama, K. Tanaka, and A. Takahara, *Macromolecules*, 28, 280-285 (1997).
[5] J. A. Forrest, K. Dalnoki-Veress, J. R. Stevens, and J. R. Dutcher, *Phys. Rev. Lett.* 77, 2002, (1996); J. A. Forrest, K. Dalnoki-Veress, and J. R. Dutcher, *Phys. Rev. Lett.* 77, 2002, (1996).
[6] L. Xie, G. B. DeMaggio, W. E. DeVries, and D. W. Gidley, *Phys Rev. Lett.* 74, 4947 (1995).
[7] K. Fukao and Y. Miyamoto, *Europhys. Lett.* 46, 649 (1999).
[8] A. D. Schwab, D. M. Agra, J.-H. Kim, S. Kumar, and A. Dhinojwala, *Macromolecules*, 33, 4903-4909 (2000).
[9] D. T. Clark and H. R. Thomas, *J. Polym. Sci. Polym. Chem. Ed.* 16, 791 (1978).
[10] G. A. Corbin, R. E. Cohen, and R. F. Barddour, *Macromolecules*, 18, 98 (1985).
[11] T. Kajiyama, K. Tanaka, and A. Takahara, *Macromolecules*, 28, 3482-3484 (1995).
[12] H. Matsuo. K. Iino, M. Kondo, *J. Appl. Polym. Sci.*, 7, 1833 (1963).
[13] R. Böhmer, K. L. Ngai, C. A. Angell, D. J. Plazek, *J. Chem. Phys.* 99, 4201 (1993).
[14] J. D. Ferry, *Viscoelastic Properties of Polymers*, 3rd Ed. Wiley and Sons, New York, 1980.