Generation and Molecular Motion of Grafted Polymethacrylate Chains on an Isotactic Polypropylene Film Surface

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ABSTRACT: Methacrylate (MA) monomers were graft copolymerized on an isotactic polypropylene (PP) film surface by the UV-irradiation method. Tethered poly(methyl methacrylate) (PMMA) and poly(butyl methacrylate) (PBMA) chains were spin-labeled to study molecular motion of the PMMA and PBMA chains in the solvent of toluene by electron spin resonance (ESR). Pinacol radicals from benzophenone (BP) as a photoinitiator, adsorbed on the PP film surface, behaved just like a dormant bonded to propagating radicals on "living" radical graft copolymerization. The chains of BP-terminated polymethacrylate (PMA) grafted to the PP were extended by sequential activation of the dormant chain ends in the presence of additional MA monomers. On the other hand, gel and sol phases of the PMA chains were produced on the PP surface. Molecular mobility of the PMA chains was strongly affected by physical structures of both PMA and PP. ESR spectra of the chains in the toluene matrices were composed of two spectra arising from two kinds of spin-labels, A- and B-labels. They were a mobile label (A) in isolated single-chain globules and smaller pinned micelles and a rigid label (B) in larger pinned micelles and the gel phase on the PP surface. The fractional amount of the mobile labels decreases with increases in grafting amount and the degree of orientation of the PP chains. It was also found that the PMMA chains were more mobile than the PBMA chains in the isolated single-chain globules on the PP surface despite the higher glass transition temperature of the PMMA in the bulk than that of PBMA. The factors for the determination of the molecular mobility of the tethered chains were discussed and related to the conformational structure.

Introduction

Many authors studied the grafted chain on polymer surface as recently reviewed by Kato et al.[1] A good introduction to tethered chains[2] and the theoretical approach to the molecular dynamics of grafted polymer chains[3] can also be found. We have studied structures and molecular motion of polymer chains tethered on poly(tetrafluoroethylene)[4] and adsorbed on silica surfaces[5−9] by ESR and NMR methods. High mobility of the tethered polymer chains were found and related to the extremely low segmental concentration and "tail" and " loop" conformational structures protruded from the surface. When one end of the polymer chains is fixed on the surfaces, aggregation behaviors of the polymer chains are much different from those for homopolymer chains. Then, loosely packed structures of the tethered chains may be formed even for the samples with high grafting ratios. Yamamoto et al.[10,11] prepared extremely high-density polymer brushes comprised of poly(methyl methacrylate) (PMMA) chains densely end-grafted on a silica substrate and clarified higher-order interactions among the grafted chains from the long equilibrium thickness of the brush in toluene. It is a very interesting problem to clarify the effect of molecular mobility of tethered chains on the segmental density. In the present paper, we prepare the samples of the PMMA and PBMA chains grafted on an isotactic polypropylene film surface. Next we elucidate molecular mobility of the grafted chains in toluene matrices and related it to physical structures of the chains, for example, gel and sol phases, and the state of aggregation as a function of segmental density. It can be considered that the bulkiness of the side groups of the grafted PMMA and PBMA chains gives different effects on the molecular mobility between the aggregation states of the low and high segmental density. Another interesting problem is the effect of the structure of the base polymer on molecular motion of the tethered chains. The polypropylene film was elongated to elucidate the effect of surface molecular orientation on the molecular mobility.

Experimental Section

Materials. An isotactic polypropylene (PP), Noblene MA-4 (product of Mitsubishi Petrochemical Co. Ltd., $M_v = 40 \times 10^4$), was used for this study. The purification of the sample, the preparation of a film, and the elongation were described in detail in our previous papers.[12,13] A sample having a stretch ratio of 5 was prepared. Methyl methacrylate (MMA) and *n*-butyl methacrylate (BMA) (Extra Pure Reagent, Tokyo Chemical Co. Ltd.) were distilled under reduced pressure. Benzophenone (BP) (Nacalai Tesque Co. Ltd.) was used as received. 2,2,6,6-Tetramethyl-4-aminopiperidine-1-oxyl (4-amino-TEMPO) (Sigma Co. Ltd.) was used as a spin-labeling reagent.

Graft polymerization of MMA and BMA to polypropylene (PP). Many investigations concerning photografting on the PE film have been published.[14] Yang and Rånby[15,16]studied photograft copolymerization of methyl methacrylate by using various photosensitizers and suggested the "living" free radical graft copolymerization by the capping of the propagating radicals. Kyozuka et al.[17] also designed the thickness of the layer of the grafted chains on the isotactic polypropylene surface and studied the molecular mobility of the chains in detail. BP was adsorbed on the film surface of PP by coating 0.5 wt % of acetone solution of BP and drying at ambient temperature. The PP film and monomer were placed in a Pyrex glass ampule. After degassing by a freeze−pump−thaw method, the ampule was sealed in a vacuum. The sealed ampule was UV-irradiated at 65 °C, and graft polymerization started. The UV-irradiation was carried out with a HLS-4002BV mercury vapor lamp (Toshiba Denki Co. Ltd.). The PP film sample grafted with MA was washed by a Soxhlet apparatus with acetone for 48 h and dried for more than 24 h at ambient temperature, and the homopolymer of MA was extracted. The

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Table 1. Change in Grafting Amount with Thickness of Sample

UV-irrad time (min)	thickness (μm)	apparent surface area (cm^2)	sample wt (mg)	increased wt (mg)	grafting ratio (wt %)	grafting (mg/cm^2)	grafting (10^{-5} mol/cm^2)
10	180	2.52	20.3	6.1	30.1	2.42	2.42
10	520	2.76	51.3	6.6	12.9	2.40	2.39
10	890	2.98	101.7	7.3	7.2	2.45	2.44

grafting amount (GA) was estimated to be weight or moles per unit surface area as follows: GA (mg/cm^2 or mol/cm^2) = $(W_{graft} - W_0)/A$. Here, W_{graft} and W_0 are weight or mole of the sample after and before grafting, and A is the apparent surface area of the film. To estimate the gel fraction of grafting layer, the film surface was scraped by a razor blade and the scrape was put and stirred in benzene solution. After all sol part of grafting chains was dissolved, the gel part was dried and weighed. The gel fraction was calculated to be percent weight of gel to the initial grafting scrape.

Spin-Labeling. To elucidate molecular motion of grafted chains, 1% of methacrylic acid monomer was added with MA monomer at graft polymerization, and the acid part of the grafted chains was spin-labeled by reaction with the 4-amino-TEMPO radical.[18,19] The grafted sample, equivalent mole of TEMPO to the acid, and dicyclohexylcarbodiimide as a dehydration reagent were stirred in *N*,*N*,-dimethylformamide solution for 72 h, washed perfectly, and dried.

ESR Measurements. ESR spectra were observed at a low microwave power level less than 0.1 mW to avoid power saturation and with 100 kHz modulation using JEOL FE3XG spectrometers (X-band) at room temperature coupled to a Microcomputer (NEC PC-9801). The film sample was placed with toluene in a Spectosil sample tube, which was connected to a vacuum line and degassed by the freeze−pump−thaw method. The signal of DPPH (1,1-diphenyl-2-picrylhydrazyl) was used as a *g*-value standard. The magnetic field was calibrated with the well-known splitting constants on Mn^{2+} in MgO.

Results and Discussion

Graft Copolymerization by Photoactivating. Figure 1 shows relationships between the grafting amount (GA) represented in units of mg/cm^2 and UV-irradiation time. GA increased linearly with increasing the irradiation time. It is well-known that photoexcited benzophenone (BP*) abstracts hydrogen from PP, and the produced PP radical initiates graft copolymerization. The increase in GA with increasing irradiation time is due to the extension of grafted chains like "living" radical polymerization. The propagating radicals are capped with pinacol radicals (BP$^{\bullet}$), and the BP-terminated MA extends through the breakage of the BP−MA bond by UV-irradiation and consumption of MA monomer. The excess BP* can also abstract hydrogen of the grafted chains and produce many branches. As a result, gel phase may be found on the film surface of PP. BP* abstracts preferentially hydrogen of PP near the film surface, and the grafted chains extend from the surface. To confirm the grafting layer on the film surface of PP, the dependency of GA on film thickness and gel fraction was studied. As shown in Table 1, the grafting amount per unit surface area for the sample prepared by UV-irradiation for 10 min is independent of the film thickness. Figure 2 shows the gel fraction of the scrap on the film surface, which is comprised of grafted MA polymer produced by the UV photoactivating copolymerization. The gel fraction for the film sample of low GA cannot be estimated because of extremely thin graft layer. These experimental facts indicate that the grafting reaction, including initiation, propagation, termination, and cross-linking of grafted chains, occurs on the film surface. In Figure 1, it is also found that GA for

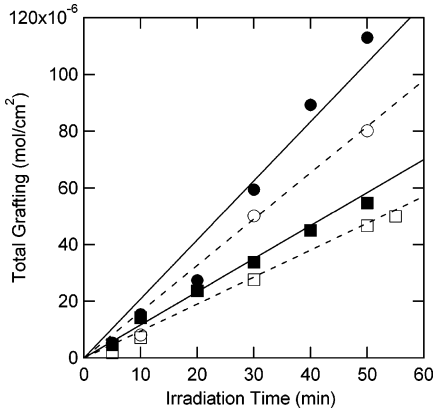

Figure 1. Dependencies of grafting amount (GA) of PMA's on PP film on irradiation time. Photografting of PMMA to nonstretched (solid circles) and stretched (solid squares) and that of PBMA to nonstretched (open circles) and stretched (open squares) were carried out by UV-irradiation at 65 °C.

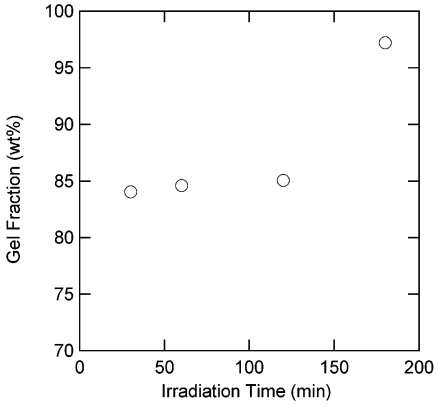

Figure 2. Gel fraction of grafted PMMA layer on PP film, generated by UV-irradiation.

the nonstretched film is larger than for the stretched film. This indicates that the orientation of PP chains near the surface makes difficult the hydrogen abstraction of BP* from PP.

Graft Copolymerization by Thermal Activating. As mentioned previously, the hydrogen abstraction of BP* from the grafted chains makes many branches on the chains and the gel phase. To prepare linear grafted chains and control the chain length, thermal copolymerization was carried out after UV-irradiation for a short time, and excess BP was washed out. The grafting reaction in the first stage was carried out by UV-irradiation for 10 min and GA of $(1.0-1.4) \times 10^{-5}$ mol/cm^2 was obtained. After the grafting, the sample was washed by a Soxhlet apparatus with acetone for 48 h and dried to take off residual monomer, BP, and homopolymer of MA. The purified film sample was placed with only monomer in the Pyrex glass ampule. After degassing, the ampule was sealed in a vacuum as the same as in the first stage. The sealed ampule was heated at 363 K and graft copolymerization in the second stage started. Figure 3 shows relationships between GA and annealing time. GA increased linearly

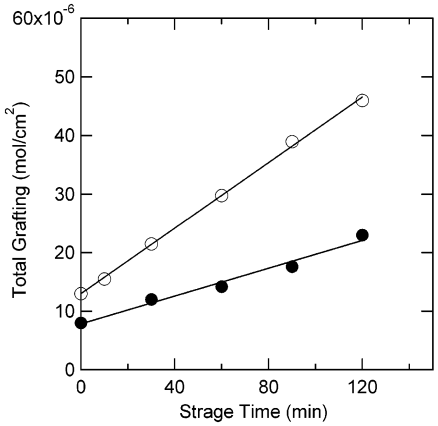

Figure 3. Dependencies of GA of PMA's on PP film on storage time. Thermal activating graft polymerization of MMA (open) and BMA (solid) at 363 K. Initial grafting were 1.3×10^{-5} and 0.8×10^{-5} mol/cm^2 for PMMA and PBMA, respectively.

with increasing the time. It is found that the grafted chains extend like "living" radical graft copolymerization.[20,21] The propagation rate of MMA is remarkably faster than that of BMA. When the sample of the photografting without BP in the first stage was heated at 363 K for a long time, no increase of weight of the sample was observed. These facts suggest that the propagating radicals are capped with BP radicals, and the BP-terminated MA extends also through the breakage of the BP−MA bond by thermal energy and consumption of MA monomer. The branching reaction on the grafted chains mentioned above can be suppressed under the second stage in the case of the thermal activating copolymerization. The linear increase of GA in Figure 3 suggests that the length of the grafted chains is well-controlled. After the second grafting, the sample was washed and graft copolymerized again by the method above. The GA also increased linearly with increasing the annealing time. When the other monomer, for example, styrene was used in the second stage, the grafting proceeded at the rate of the propagating. These results also suggest that the grafted chains extend like "living" radical copolymerization.

Molecular Motion of Grafted PMMA Chains in the Solvent of Toluene. Figure 4 shows the GA dependence of ESR spectrum of spin-labeled PMMA grafted on the film surface of PP, observed at 298 K in toluene matrices. In general, the outermost splitting of the main triplet spectrum due to hyperfine coupling caused by nitrogen nucleus narrows with an increase in mobility by the averaging of the anisotropic interaction between electron and nucleus. The complete averaging gives rise to the isotropic narrowed spectrum. ESR spectra in Figure 4 are composed of two spectra from two kinds of spin-labels, mobile label (A) and rigid label (B) as indicated in Figure 4. The outermost splitting width between the extreme peaks due to A- and B-labels are large and small, respectively. The grafted chains were generated by UV photoactivating copolymerization. The gel fraction is somewhat large for the sample of high GA, as shown in Figure 2. The film samples were soaked in toluene, where the grafted chains in the sol phase were dissolved and the gel phase were swelled with toluene. The narrow triplet spectrum due to A-labels, observed for the sample of low GA, was hardly observed for the sample of higher GA than 5.95 mg/cm^2. A broad spectrum due to B-label appears for the sample of GA = 1.05 mg/cm^2, and its intensity increases with

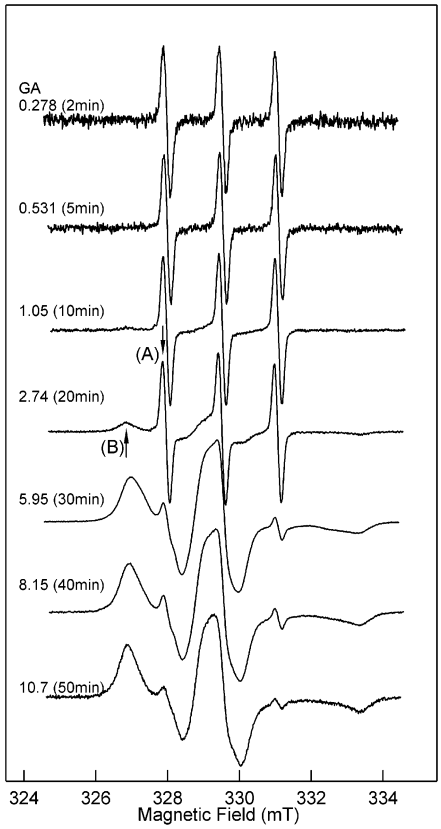

Figure 4. GA-dependent ESR spectra of PP-*g*-PMMA by UV photoactivating polymerization which are observed at 298 K. The irradiation times are shown in the parentheses. GA's in the figure are represented in units of mg/cm^2.

an increase in GA. The two spectral components are observed for the samples in a wide range of GA. This is a reflection of a distribution of correlation time of molecular motion, arising from a heterogeneous structure of the grafted chains on the PP surface, for example, the distribution of chain length and segmental density. As a result, the aggregation structure has a broad distribution of free volume size. When the length of the grafted chain for the sample of GA (0.278 and 0.531 mg/cm^2) is short, and the chains cannot contact each other, the chains collapse separately, forming individual single chain globules[22] in the toluene matrices. The spin-labels bonded to the grafted chains move rapidly at random as A-labels. When molecular weight increases and chain extends with an increase in GA, the grafted chains begin to contact with each other and fuse to form pinned micelles[22] due to the competition between the attractive force and the grafting constraints, at moderate segmental densities. In the pinned micelle, one end of the grafted chain is fixed on the PP surface, and other segments containing another end are entangled with those of other grafted chains. The gel phase can be also produced by the branching and crosslinking reactions. The molecular mobility of the grafted chains in the micelles and gel phase is too low, and the spin-labels bonded to the chains behave as B-labels. These interpret that two components of ESR spectra have a strong dependence on GA. The narrow spectrum can be assigned to be mobile label (A) bonded to the segment of the grafted chain, which has a low segmental density and can move rapidly as a free rotation. All spin-labels trapped in the sol phase are not necessarily A-labels. The spectrum due to the labels is still detected for the sample of high GA, where the mobile fraction

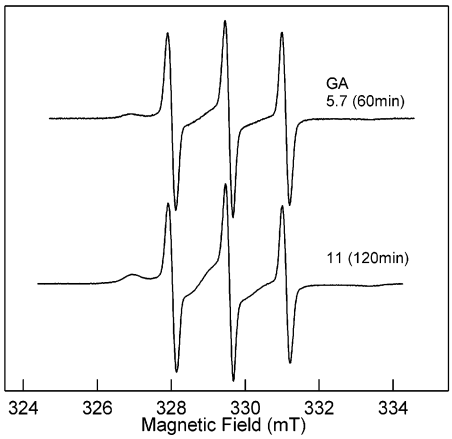

Figure 5. GA-dependent ESR spectra of PP-*g*-PMMA by UV thermal activating polymerization. The storage times are shown in the parentheses. GA's in the figure are represented in units of mg/cm^2.

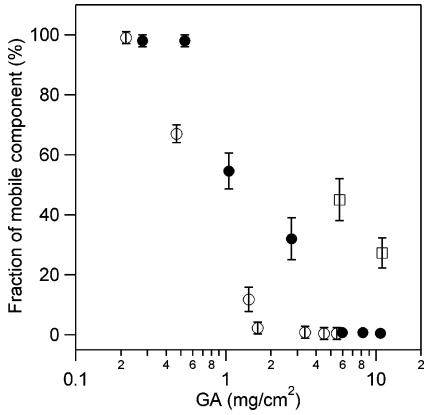

Figure 6. Dependency of fraction of mobile component of ESR spectra on GA. Mobile fraction of PMMA grafted on the PP (solid circle), PMMA grafted on the stretched PP (open circle) by photoactivating, and PMMA grafted on the PP by thermal activating (open square).

(the fractional concentration of A-label) is extremely low in comparison with the sol fraction (1 − gel fraction) as shown in Figure 2. A part of labels in the sol phase behaves as B-labels. Figure 5 shows ESR spectra of spin-labeled PMMA grafted on the film surface of PP, by the thermal activating copolymerization, where the branching reaction is suppressed and the gel fraction is very low. Surprisingly, the narrow triplet spectrum due to A-labels appears to some extent in even a high GA value of 11 mg/cm^2 in the case of the thermal activating sample. This indicates that linear PMMA chains grafted on PP surface are formed and move rapid in the toluene matrices. It is also found that the molecular mobility of A-labels decreases and the fractional intensity of B-labels increases with an increase in GA. The rotational correlation time (τ_c) of labels is calculated simply by Kivelson's,[23] theory as indicated in Table 2. The correlation time increases with an increase in GA. These suggest that the extension of the grafted chains increase the dimension of single chain globules, and the pinned micelles are partially generated. What are important factors for the determination of segmental mobility of chains tethered on PP film surface? The segmental mobility is reflected on mobile (A) or rigid (B) labels and the rotational correlation time, τ_c, of the labels. In general, rotational correlation time, τ_{co}, of segments in the single-chain globules is a function of segmental density related to molecular weight and solubility parameter with solvent. Zhulina et al.[24] constructed a diagram of states for the case of a system of polymer chains end-grafted to a planar surface. The degree of polymerization, N, and grafting density, σ, determine the states. The single globules also have a radius of $R_s \cong N^{1/3}$ and the segmental density, $\rho \cong N/R_s^3$, which is independent of the length of the grafted chain. As a result, the increase of the correlation time for the mobile (A) labels with an increase in GA is caused by their contact of the single globules. The structure of the state where the globules contact and entangle with each other, and the segments still take a free rotation can be represented as in a smaller pinned micelle. Flexibility of PMMA grafted chains and surface mobility of PP also affect molecular motion of the segments. Mobile labels convert to rigid B-labels when τ_{co} increases and reaches to a crossover time, τ_{coc}. Then, the grafted chains aggregate by an increase in chain length. The time τ_{coc} can be considered to be a correlation time where the free rotation of the segments starts to be inhibited. The state of aggregation, where the free rotation is inhibited, can be represented as a large pinned micelle. Mobile and rigid labels in the pinned micelles must be trapped in the small and large pinned ones, respectively. The correlation times of the chains in the micelles are shorter and longer than the crossover time, τ_{coc}. The aggregation state of the grafted chains on the film surface has a broad distribution of the single globules and the pinned micelles. For the evaluation of the molecular mobility related to the aggregation state, the ESR spectrum was decomposed, and the spectral intensities of the mobile and rigid components were calculated. The fractional intensity of the spectrum due to A-labels (the mobile fraction) was plotted for GA in Figure 6. The fractions decrease with an increase in GA. The pinned micelles begin to be formed with the chain extension and the increasing of the grafting cites and the B-labels with the fraction of 50% appear for the nonstretched sample of GA = 1.05 mg/cm^2 (●) in the case of photoactivating copolymerization. The high fractions of the fast component for the thermal activating sample (□) are distinctly found. The fractions for the stretched sample (○) are lower than for the nonstretched sample in the case of photoactivating copo-

Table 2. Correlation Time (τ_c) of Mobile Spin-Label for Various Samples at 298 K

	photoactivating		thermal activating	
samples	grafting (mg/cm^2)	τ_c (s)	grafting (mg/cm^2)	τ_c (s)
nonstretched PP PMMA graft	0.278	1.1×10^{-11}	5.70	2.1×10^{-10}
	0.531	4.4×10^{-11}	11.0	3.5×10^{-10}
	1.05	4.6×10^{-11}		
	2.74	1.4×10^{-10}		
stretched PP PMMA graft	0.216	6.9×10^{-11}		
	0.469	9.9×10^{-11}		
	1.42	4.4×10^{-10}		
nonstretched PP PBMA graft	0.74	2.5×10^{-10}		

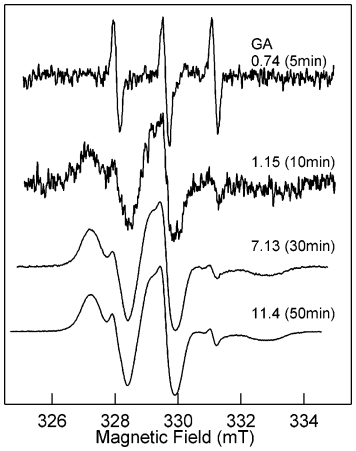

Figure 7. GA-dependent ESR spectra of PP-*g*-PBMA by UV photoactivating polymerization. The irradiation times are shown in the parentheses. GA's in the figure are represented in units of mg/cm^2.

lymerization. The highly oriented main chains slow down the molecular mobility of the grafted PMMA chains because of the low surface mobility of PP. The correlation time, τ_{co}, of the segments of the single-chain globules reaches τ_{coc} at lower GA. The longer correlation time for the stretched sample than that in the non-stretched sample was also found as indicated in Table 2.

Molecular Motion of Grafted PBMA Chains in Toluene Matrices. Figure 7 shows the GA dependence of ESR spectra of spin-labeled PBMA grafted on the film surface of PP, observed at 299 K in the toluene matrices. The grafted chains were generated by UV photoactivating copolymerization. The mobile labels (A) were observed only for the sample of GA = 0.74. mg/cm^2 in Figure 7. The correlation time is longer than one for the PMMA grafted chains of GA = 1.05 mg/cm^2 as indicated in Table 2. The intensity of the narrow spectrum due to the A-labels is very weak for the PBMA sample of GA higher than 1.15 mg/cm^2 for the PBMA sample, whereas the spectrum due to A-labels is weak for the PMMA sample of higher than 5.95 mg/cm^2. The correlation time of the mobile PBMA labels is ca. 6 times longer than the mobile PMMA labels as indicated in Table 2. These results suggest that the PMMA chains are more mobile than the PBMA chains in the isolated single chain globules on the PP surface. The solubility of polymer chains with toluene affects the molecular mobility of chains in the solvent. The Flory−Huggins interaction parameters, $\chi_{polymer-solvent}$, of polymer and solvent should be considered. $\chi_{PMMA-toluene} = 0.58$ and $\chi_{PBMA-toluene} = 0.17$ are tabulated in the *Polymer Handbook*.[25] These values of χ parameters are obtained for polymer volume fraction of 0.6 and at 50 °C. The volume fraction of the grafted chain to toluene is not 0.6, and the experiments were carried out at ambient temperature in this study. But the difference between $\chi_{PMMA-toluene}$ and $\chi_{PBMA-toluene}$ is meaningful for the discussion of molecular motion of PMA surrounded by the solvent. Toluene is a good solvent of PBMA, the segments of which extend largely in the solvent in comparison with PMMA. The PMMA chains grafted on the PP surface move more rapid despite the lower solubility. Therefore, it can be concluded that the PMMA chains in the single-chain globules on the PP surface are more mobile than the PBMA chains though the glass transition temperature of the PMMA, T_g (378 K), is higher than that of PBMA (293 K) in the bulk. For instance, a PMMA chain having small side chains is more flexible than a bulky PBMA chain in the single-chain globules. Matsuoka et al.[26,27] proposed a domain where the number of conformers moved cooperatively. If equilibrium can be achieved at a low-temperature limit, 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 the domain is 1. The weak interchain interaction in the isolated single chain globules give a situation like the independent relaxation of each conformer. Therefore, the molecular mobility of the grafted single-chain globules depends on the conformer size. Matsuoka et al.[26,27] also defined the M_c as molecular weight (M_w) of monomer unit divided by the number (N_c) of conformer in the unit. The conformer size of PMMA, 50, can be seen to be smaller than that of PBMA, 71. The fact suggests the higher flexibility of PMMA chains without interchain interaction for the single-chain globule. On the other hand, the outermost splitting of the rigid label (B) of PBMA in Figure 7 is smaller than that of PMMA in Figure 4. The rotational correlation time of the rigid label is also calculated approximately by Freed's equation using the moderate jump model.[28] Deviation of extreme separation from the value of rigid state was used to calculate the correlation time. It is found that the correlation time of the PBMA chains, 7.8×10^{-9} s, is shorter than that of the PMMA chain, 2.1×10^{-8} s, for the same GA of 3.3 mg/cm^2. This indicates that the PBMA chains in the rigid region are mobile in comparison with the PMMA because the segments contact with each other, and bulky side chains of PBMA make larger free volume even in the swelled state containing the solvent. The same effect of highly oriented PP chains on mobility of the grafted PMMA chains is elucidated for the PBMA chains. ESR spectra of spin-labeled PBMA grafted on the film surface of the stretched PP by the photoactivating copolymerization have no narrow component due to mobile labels (A) because of the rigidity of PBMA chains and the orientation of the PP chains.

Conclusion

1. Polymethacrylate (PMA) grafted chains are generated on the surface of the isotactic PP by the UV-irradiation method. (a) The grafting amount (GA) increases linearly with irradiation time, and gel phase is partially formed in the case of photoactivating copolymerization. (b) GA also increases linearly with storage time just like "living" radical graft polymerization in the case of thermal activating copolymerization.

2. The molecular mobility of the grafted PMA chains is strongly affected by physical structure of PMA and PP chains. (a) The correlation time of the segment increases with increases in chain length and the degree of aggregation of the grafted chains. A-labels (mobile) convert to B-labels (rigid) in toluene matrices with an increase in GA when the free rotation of the segments is inhibited. The experimental fact reflects the change of the aggregation of the single-chain globules to the large pinned micelles. The PMMA chains on the surface of the PP are more flexible than the PBMA chains because of the weak intrachain interaction of the PMMA chains. (b) The orientation of the PP chains slows down the molecular mobility of the grafted PMA chains.

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