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Nanoscopic Aggregation in Random Copolymer Bulk Films Studied with Photochemical Hole Burning and Transmission Electron Microscopy

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ABSTRACT: Nanoscopic aggregation in random copolymers of methyl methacrylate (MMA) with *n*-butyl methacrylate (*n*-BMA) or benzyl methacrylate (BzMA) in bulk films has been studied for the first time at low temperatures by using photochemical hole burning (PHB) spectroscopy for tetraphenylporphine (TPP) dispersed in the copolymers and also with transmission electron microscopy (TEM). Temperature cycle experiments with PHB were carried out for the copolymers with different ratios of comonomer groups. The increases in hole widths due to structural relaxation of butyl groups or benzyl groups in the copolymers of *n*-BMA or BzMA with MMA were much larger than those expected for hypothetical systems where MMA and comonomer groups with the corresponding molar ratios are randomly dispersed. The results have been attributed to the nanoscopic aggregation of *n*-BMA or BzMA units with the preferential inclusion of TPP within them in the films. PHB spectroscopy provides a new tool for studying nanoscopic aggregation larger than 2.3 nm in transparent random copolymer bulk films. The nanoscopic aggregation of MMA-rich domains with the diameter of 20−30 nm in a random copolymer bulk film of MMA with BzMA has also been ascertained with TEM measurements. A TEM picture of a polymer blend film of PMMA and PBzMA (1:1) showed phase separation with PBzMA-rich domains of ca. 500 nm diameter.

Introduction

Two kinds of high-molecular-weight homopolymers consisting of chemically different monomeric units are usually incompatible, and their blends, when cooled from the melt or cast from solution, undergo macroscopic phase separation with segregation of the components at equilibrium. In cases of block copolymers, if the molecular weights of different blocks are sufficiently high, the mutual incompatibility of those blocks leads to microphase separation with a characteristic morphology existing throughout the samples.[1,2] The morphology of the microphase separation is revealed by the optical micrograph,[3,4] transmission electron microscopy (TEM),[5−7] small-angle X-ray scattering (SAXS),[8] and small-angle neutron scattering (SANS).[8] In addition to popular morphologies, such as lamellae, cylinders, and spheres, ordered bicontinuous morphologies, such as OBDD and gyroid, and mesh morphology of microdomain structures have been detected in block copolymer systems.[9]

On the other hand, a random copolymer is the one where the different comonomers are covalently bonded in the main chain randomly, which gives the idea that the random copolymer behaves like a microscopically homogeneous polymer and its film exhibits no microphase separation. However, as for an amphiphilic random copolymer containing hydrophilic and hydrophobic groups, if the content of hydrophobic units in the copolymer is sufficiently high, even a single polymer molecule will adopt micelle-like microphase structure in aqueous solution where the hydrophobic units form an interior domain surrounded by a charged outer layer.[10] Morishima et al.[11] reported the nanoscopic aggregation in bulk films of the amphiphilic random copolymers of sodium 2-(acrylamido)-2-methylpropanesulfonate (AMPS) with a comonomer carrying bulky hydrophobic side-chain lauryl (LA) groups for the first time by using TEM. However, it has been widely supposed for long time that bulk films of random copolymers consisting of two miscible hydrophobic comonomers are homogeneous even on the nanometer scale.

In our previous papers,[12] we extended the photochemical hole burning (PHB) study for the first time from simple amorphous polymers to a polymeric nano-organized system. In a manner similar to our studies of PHB for amorphous polymers,[13−16] temperature cycle experiments have been performed in order to investigate thermal stability of holes and structural relaxation in host matrices. Highly constrained microenvironments around free-base tetraphenylporphine (TPP) groups in amphiphilic random terpolymers containing sodium sulfonate (A) groups with cyclododecyl (CD) or lauryl (LA) groups together with a small amount of TPP groups were studied at low temperatures with PHB. The terpolymers were embedded in poly(vinyl alcohol) (PVA). Only the terpolymer with CD groups formed unimacromolecular micells (unimers) in the polymer matrix.[12a] Then the terpolymers with controlled radii of the unimers with CD groups were prepared and embedded in PVA.[12b] The hole widths of the unimers in PVA were independent of the unimers radii, which suggested the structural relaxation detected by PHB temperature

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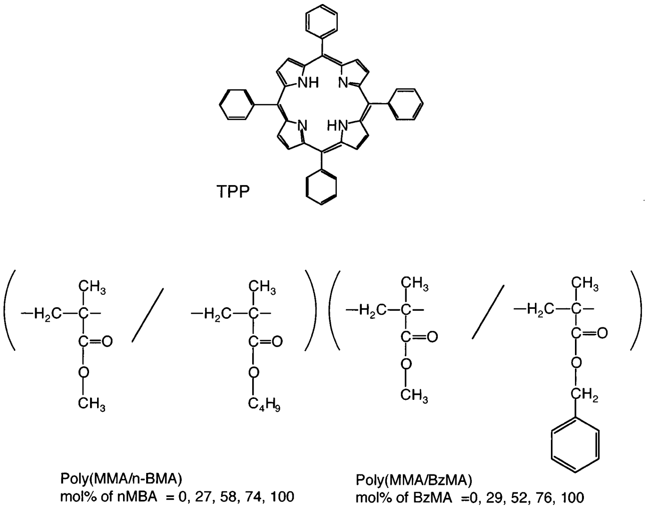

Figure 1. Chemical structures of the random copolymers, homopolymers, and a chromophore used in the present study.

cycle experiments was effective within 2.3 nm.[12b] The effective distance within which the porphyrin molecule can sense the structural relaxation of surrounding polymer chains was also ascertained to be 2.5 nm by PHB of dendrimers with a TPP core.[17] We confirmed that PHB is very useful for studying the nanoenvironments around the chromophores. The nanoscopic aggregation in bulk films of the amphiphilic random copolymers already reported by TEM[11] has been recently confirmed by PHB temperature cycle experiments.[18] The PHB measurements for the detection of nanoscale aggregation are based on the difference in structural relaxation of comonomer units and are independent of whether any of comonomer units can be dyed for TEM observation. Thus, we can say that PHB is very attractive tool for studying nanoscopic aggregation in bulk films of the random copolymers and can be applied to wide varieties of comonomer combinations.

The objective of the present paper is to study with PHB the nanoscopic aggregation in the bulk films of random copolymers of hydrophobic comonomers. The random copolymers of methyl methacrylate (MMA) with *n*-butyl methacrylate (n-BMA) or benzyl methacrylate (BzMA) in various molar ratios were prepared. We observed the structural relaxation behavior from thermally induced irreversible changes in hole profiles during temperature cycle experiments. The existence of nanoscopic aggregation in these random copolymer films has been revealed for the first time by using the PHB technique. The nanoscale (in 20−30 nm) aggregates of MMA-rich phase in a random copolymer of MMA with BzMA were also ascertained by TEM with RuO_4 dyeing. Hydrophobic alkyl ester groups in copolymers are usually difficult to be distinguished from each other by dyeing, and hence the nanoscopic aggregation, if any, is hardly detected by the usual techniques other than PHB. Thus, we propose a PHB technique to detect the nanoscopic aggregation of the random copolymer films with hydrophobic comonomer groups.

Experimental Section

Polymer Preparation. Figure 1 shows chemical structure of the samples in the present study. MMA, *n*-BMA, and BzMA were provided by Tokyo Kasei and were distilled in a vacuum after stirred with CaH_2. The copolymers of MMA with ca. 25, 50, and 75 mol % *n*-BMA or BzMA were prepared by free radical copolymerization with 2,2′-azobis(isobutyronitrile) (AIBN). These copolymers are denoted as poly(MMA/*n*-BMA) (73/27, 42/58, 26/74) and poly(MMA/BzMA) (71/29, 48/52, 24/76) ($M_w = 2.8 \times 10^5$, 2.2×10^5, 2.8×10^5, 1.2×10^5, 3.5×10^5, and 1.5×10^5, respectively). Poly(MMA/*n*-BMA) and poly(MMA/BzMA) were purified by reprecipitation from dichloromethane into a large excess of methanol. Homopolymers of MMA, *n*-BMA, and BzMA ($M_w = 2.2 \times 10^5$, 3.1×10^5, and 1.8×10^5, respectively) were prepared with radical polymerization initiated with AIBN. PMMA, P*n*-BMA and PBzMA were purified by reprecipitation from dichrolomethane into a large excess of methanol. The weight-average molecular weights, M_w, of the copolymers were measured with GPC (Jasco BIP-I with Shodex AC-80M/S). The comonomer compositions in the copolymers were determined by NMR (JEOL JNM-GX270 FT-NMR). The glass transition temperatures, T_g, of the homopolymers and random copolymers were measured with a differential scanning calorimeter (Perkin-Elmer DSC II).

Film Preparation for PHB Measurements. Tetraphenylporphine (TPP) (Tokyo Kasei) was used as supplied. The TPP-doped sample films, TPP/PMMA, TPP/poly(MMA/*n*-BMA), TPP/poly(MMA/BzMA), TPP/P(*n*-BMA), and TPP/PBzMA were prepared by solvent casting from dichloromethane. The concentration of TPP in the films was on the order of 10^{-3} mol kg^{-1}. TPP/PMMA, TPP/poly(MMA/*n*-BMA), and TPP/P(n/BMA) were dried under vacuum at 100 °C for about 4 h to eliminate the residual solvent. TPP/poly(MMA/BzMA) and TPP/PBzMA were dried under vacuum at ambient temperature.

PHB Measurements. Samples were placed in an optical cryogenic refrigerator (Sumitomo SRD204). Transmission spectra were obtained by scanning a 1 m monochromator (Jasco CT100C) and detecting the transmitted light of a halogen lamp with a photomultiplier (Hamamatsu R943−02) together with a lock-in amplifier (Jasco LA126W). The holes were burnt by the irradiation with an Ar^+ laser (Coherent, Innova 70) pumped ring dye laser (Coherent, 699-01) with 4-(dicyanomethylene)-2-methyl-6-(4-(dimethylamino)styryl)-4*H*-pyran (DCM). The experiments were controlled by and data-stored in a personal computer. Spectra were corrected with the apparatus spectral response. Fundamentals of the PHB measurements are similar to the previous cases.[14,15] Laser irradiation was performed for about 20 min with a low power of about 0.075 mW/cm^2 until deep holes were obtained. When the zero-phonon hole was accompanied by a side hole or the zero-phonon hole was not so deep, the hole profile was difficult to be detected at high temperatures. So we irradiated a deep hole without making any side hole. After burning the hole, irreversible hole decay was measured with temperature cycle experiments.[14] The hole widths were estimated from Lorentzian fitting of the hole profiles. The error range of measured hole widths was usually 5% but was sometimes became about 10%.

TEM Measurements. Random copolymers of BzMA have a possibility to be dyed with RuO_4 for transmission electron microscopy (TEM) measurements. So, a random copolymer film of poly(MMA/BzMA) (50/50) prepared by photoinitiated free-radical copolymerization of MMA with BzMA in the presence of AIBN was used for TEM measurements with RuO_4 dyeing. Homopolymers of PMMA (MRC Acrypet) and PBzMA prepared by free-radical polymerization with AIBN and 2,2′-azobis-(isovaleronitrile) as well as their polymer blend (1:1) were also used for TEM measurements as reference samples. The TEM observation of 2.0×10^4 and 1.0×10^5 magnifications was carried out for RuO_4-dyed films of ca. 100 nm thickness with a Hitachi H-7600 type transmission electron microscope.

Observation with Fluorescence Optical Microscope. Polymer blend films of PMMA with P(*n*-BMA) or PMMA with PBzMA which contain ca. 1×10^{-3} mol kg^{-1} TPP were prepared by spin-coating from dichloromethane. The fluorescence microscope observation was carried out with an Olympus BX60F5 fluorescence microscope for the above polymer blend films containing TPP as well as the random copolymer films containing TPP.

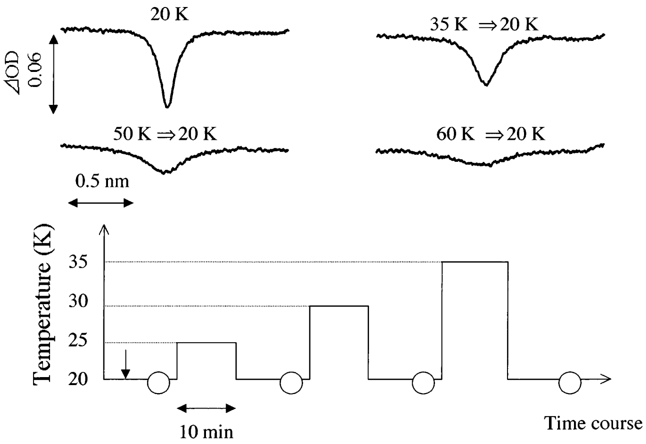

Figure 2. Typical hole profiles during a temperature cycle experiment of PHB for TPP/poly(MMA/*n*-BMA) (50/50). Procedure of the temperature cycle experiment is also shown. ↓ corresponds to burning a hole, and ○ corresponds to measuring the hole profile.

Results and Discussion

Structural Relaxation Detected by Photochemical Hole Burning. Typical hole profiles during a temperature cycle experiment for TPP/poly(MMA/*n*-BMA) (42/58) are presented in Figure 2. The temperature cycle experiments were performed as follows. After burning a deep hole at 20 K the hole profile was measured. Then the sample was annealed for 10 min at a certain excursion temperature. We cooled the sample again to 20 K, and its hole profile was measured again. This process was repeated with increasing excursion temperatures. The excursion temperature dependence of the increase in hole width, $W(T) - W(20)$, was calculated, where $W(20)$ is the initial hole width at 20 K and $W(T)$ is the hole width measured at 20 K after cooling from an annealed temperature, T.

When we consider the case where matrix and dopant molecules interact via permanent dipole moments, the increase in hole width, ΔW, can be described by[19,20]

$$\Delta W = \frac{2}{3}\pi^2 \rho(T)\beta \qquad (1)$$

where $\rho(T)$ is the number density of the matrix unit which causes structural relaxation at a certain temperature, T, in the sample. The parameter β is given by eq 2.

$$\beta = \frac{2\Delta\mu\mu_M}{4\pi\epsilon_0 hc}$$

where $\Delta\mu$ denotes the difference vector between the static dipole moments of a dye molecule in its excited and ground states, μ_M is the dipole moment of the surrounding matrix unit, ϵ_0 is the permittivity of vacuum, h denotes Planck's constant, and c is the velocity of light in a vacuum. In the case where MMA and *n*-BMA units are randomly dispersed, the values of β for MMA and *n*-BMA are about the same as those for their homopolymers, PMMA and P(*n*-BMA), while $\rho(T)$ of MMA or the *n*-BMA unit corresponds to $\rho(T)$ in PMMA or P(*n*-BMA) multiplied by its fraction in the copolymer, respectively. So in a hypothetical system, where MMA and *n*-BMA are randomly distributed without aggregation or TPP is randomly dispersed in both MMA and *n*-BMA nanodomains even when there is some aggregation, the increase in hole width should be the addition of the increases in hole width in PMMA and P(*n*-BMA) multiplied by each fraction in the copolymer.

One can, in principle, expect some temperature dependence of the change in hole width due to the spectral diffusion as measured in temperature-cycling hole burning experiments. Kohler et al.[21] carried out hole burning experiments for the different types of glasses, namely alcohol glasses, hydrocarbon glasses, and PMMA, and interpreted the results in terms of well-known spectral diffusion models, in which they introduced a freezing condition to account for thermal irreversibility. There are a tunneling TLS regime for low temperatures and an activated regime for high temperatures. In the tunneling regime the broadening is linear to T, whereas in the activated regime it increased with $T^{3/2}$. However, the temperature dependence of the change in hole width during temperature cycle experiments for amorphous polymer systems up to 60−120 K is determined by pertinent relaxation processes of local chains. Hence, in most cases no unified power law can be assumed against temperature. Tanaka et al.[14] investigated the temperature cycle experiments for various TPP/poly(alkyl methacrylate)s systems. In the case of poly(ethyl methacrylate) (PEMA), the hole width begins to broaden at 17 K,[14c] reflecting the beginning of rotation at 17 K of the ester ethyl group of PEMA around the C−O bond (δ-relaxation in PEMA). A loss maximum in dielectric relaxation (110 Hz−10 kHz)[22] and mechanical relaxation (below 0.5 Hz)[23] was reported at around 50 K for PEMA. Correspondingly, the hole width change shows a plateau from 50 to 70 K and increases again above 70 K for PEMA[14a,b] because the results of PHB temperature cycle experiments give the integrated amounts of relaxation processes between burning temperature and excursion temperature in frequencies of very wide range. This case could never be fitted to $T^{3/2}$ dependence. This is just because the temperature dependence is determined by certain relaxation processes, namely the rotation of the ester ethyl group in the case of PEMA. So in the present study we did not fit the results to any power law. First we draw the lines of the temperature dependence of the increase in hole widths of the homopolymers smoothly. Then we calculated the hypothetical system using an additivity law as to the molar fractions of the comonomer units. The values of the increase in hole width for thus calculated hypothetical systems are shown with intermittent lines in the following figures.

Enhanced Increase in Hole Width in Random Copolymer Bulk Films. Figure 3 shows the excursion temperature dependence of the increase in hole width, $W(T) - W(20)$, for TPP/P(*n*-BMA), TPP/poly(MMA/*n*-BMA) (26/74, 42/58, 73/27), and TPP/PMMA measured with temperature cycle experiments. The intermittent lines represent the hypothetical systems where MMA and *n*-BMA units are randomly dispersed homogeneously with the respective ratios of 26:74 (upper), 42:58 (middle), and 73:27 (lower). The increase in hole widths at a certain temperature in all the TPP/poly(MMA/*n*-BMA) films is markedly enhanced compared to those in the corresponding hypothetical systems. So in these systems MMA and *n*-BMA monomer units are considered to form aggregates with the size of at least 2.3 nm. A nanoscopic aggregation is suggested to provide MMA-rich and n-BMA-rich nanodomains. The

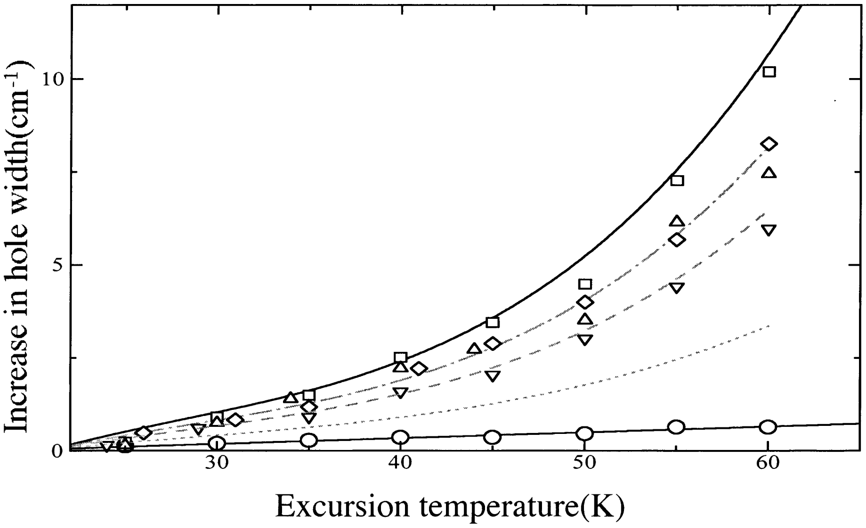

Figure 3. Excursion temperature dependence of the increase in hole width burnt at 20 K: (□) TPP/P(*n*-BMA) (3.4 cm^{-1}), (◇) TPP/poly(MMA/*n*-BMA) (26/74) (2.4 cm^{-1}), (△) TPP/poly(MMA/*n*-BMA) (42/58) (2.4 cm^{-1}), (▽) TPP/poly(MMA/*n*-BMA) (73/27) (2.7 cm^{-1}), (○) TPP/PMMA (2.3 cm^{-1}). The values in parentheses correspond to $W(20)$. The intermittent lines correspond to hypothetical systems where MMA and *n*-BMA units are randomly located with the ratios of 26:74 (upper), 42:58 (middle), and 73:27 (lower).

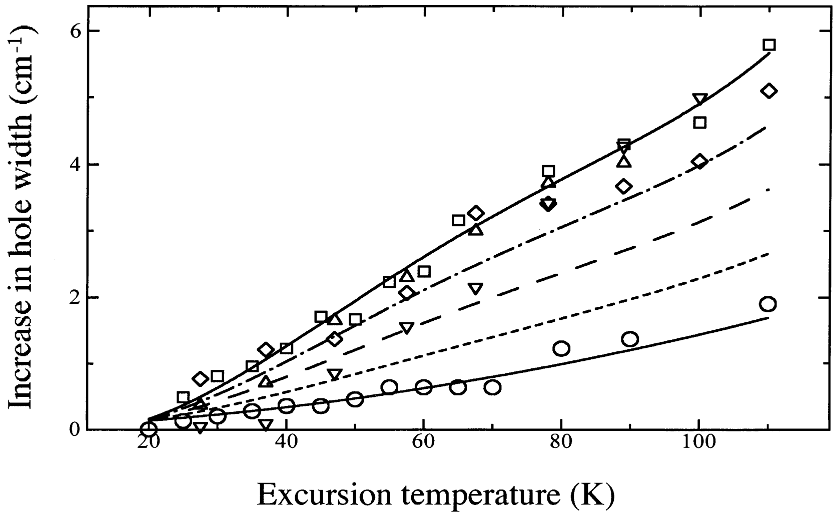

Figure 4. Excursion temperature dependence of the increase in hole width burnt at 20 K: (□) TPP/PBzMA (3.6 cm^{-1}), (◇) TPP/poly(MMA/BzMA) (24/76) (6.1 cm^{-1}), (△) TPP/poly(MMA/BzMA) (48/52) (6.3 cm^{-1}), (▽) TPP/poly(MMA/BzMA) (71/29) (4.9 cm^{-1}), (○) TPP/PMMA (2.3 cm^{-1}). The values in parentheses correspond to $W(20)$. The intermittent lines correspond to hypothetical systems where MMA and BzMA units are randomly located with the ratios of 24:76 (upper), 48:52 (middle), and 71:29 (lower).

TPP is considered to be in the *n*-BMA-rich nanodomain. The possibility of the deviation of $W(T) - W(20)$ from the hypothetic systems due to cooperative motion of MMA units affected by the presence of *n*-BMA units or vice versa like in the case observed at higher temperatures for copolyesters[24] would be excluded in the present case by the fact that MMA units have no relaxation process between 20 and 60 K, and each structural relaxation causing the increase in hole width at very low temperatures has been related to certain concrete atomic group motions which begin to rotate or librate at certain temperatures.[14a]

According to the Flory–Huggins theory,[25] the entropy part of the mixing energy of the polymer is nearly zero due to the large degree of polymerization. On the other hand, the enthalpy part of the mixing energy of the polymer is positive in usual cases without some special interaction such as hydrogen bonding, charge transfer complex formation, or electrostatic interaction. That is why we cannot expect the mixing energy of the polymer to be negative when different polymers are usually mixed. In the case of the present random copolymer bulk films, the large degree of polymerization also holds, and there is no special interaction other than the van der Waals one among monomer units. So, as for the mixing energy in the random copolymer bulk films, nanoscopic aggregation would be energetically more stable than the homogeneous distribution. Of course, comonomer units are randomly bonded to each other, and they cannot separate far from each other. Thus, like the amphiphilic random copolymers, the random copolymer films of poly(MMA/*n*-BMA) also have a possibility to exhibit nanoscopic aggregation.

Figure 4 shows the excursion temperature dependence of the increase in hole width, $W(T) - W(20)$, of TPP/PBzMA, TPP/poly(MMA/BzMA) (24/76, 48/52, 71/29), and TPP/PMMA measured with temperature cycle experiments. The intermittent lines represent the hypothetical systems where MMA and BzMA are randomly dispersed with the respective ratios of 24:76 (upper), 48:52 (middle), and 71:29 (lower). The increase in hole widths at a certain temperature in all the TPP/

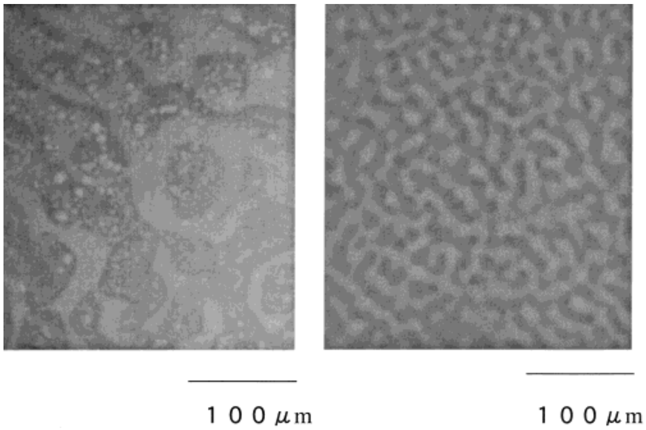

Figure 5. (a) Fluorescence micrograph of a TPP-doped polymer blend of PMMA with P(*n*-BMA) with the ratio of 3:1. (b) Fluorescence micrograph of a TPP-doped polymer blend of PMMA with PBzMA with the ratio of 1:3 which was annealed at 100 °C for 12 h.

poly(MMA/BzMA) is enhanced compared to those in the corresponding hypothetical systems. So in these systems MMA and BzMA units are considered to form aggregates. The nanoscopic aggregation is suggested to provide MMA-rich and BzMA-rich nanodomains. The TPP is considered to be in the BzMA-rich nanodomain.

In the above discussion on the PHB experiments, we implied that TPP is located in the *n*-BMA-rich or BzMA-rich nanodomain of the random copolymer bulk films. To ascertain in which nanodomain TPP molecules are more easily dissolved, we prepared polymer blend films composed of two homopolymers (PMMA with P(*n*-BMA) or PBzMA) and fluorescent TPP and investigated with a fluorescence optical microscope in which microdomain of the polymer blends TPP is more easily dissolved. Figure 5a shows a fluorescence micrograph of a TPP-doped polymer blend of PMMA with P(*n*-BMA) with the weight ratio of 3:1, where the deeply colored region indicates the domains of P(*n*-BMA) with fluorescing TPP. We have ascertained that the area of the fluorescing red domain increases with increasing composition of P(*n*-BMA), confirming that TPP is dissolved in P(*n*-BMA) region easily compared to the PMMA region. The P(*n*-BMA) region is less polar with more flexible side chains than the PMMA region, providing more easy dispersion of TPP in the P(*n*-BMA) region. Fluorescence micrographs of the random copolymers of poly(MMA/*n*-BMA) showed no domain structure of micrometer scale.

Figure 5b shows a fluorescence micrograph of a TPP-doped polymer blend of PMMA with PBzMA with the weight ratio of 1:3, which was annealed at 100 °C for 12 h. The deeply colored region in the micrograph indicates PBzMA domains with fluorescing TPP. We could not see any phase separation in the fluorescence micrographs of the blends with other polymer ratios (i.e.,

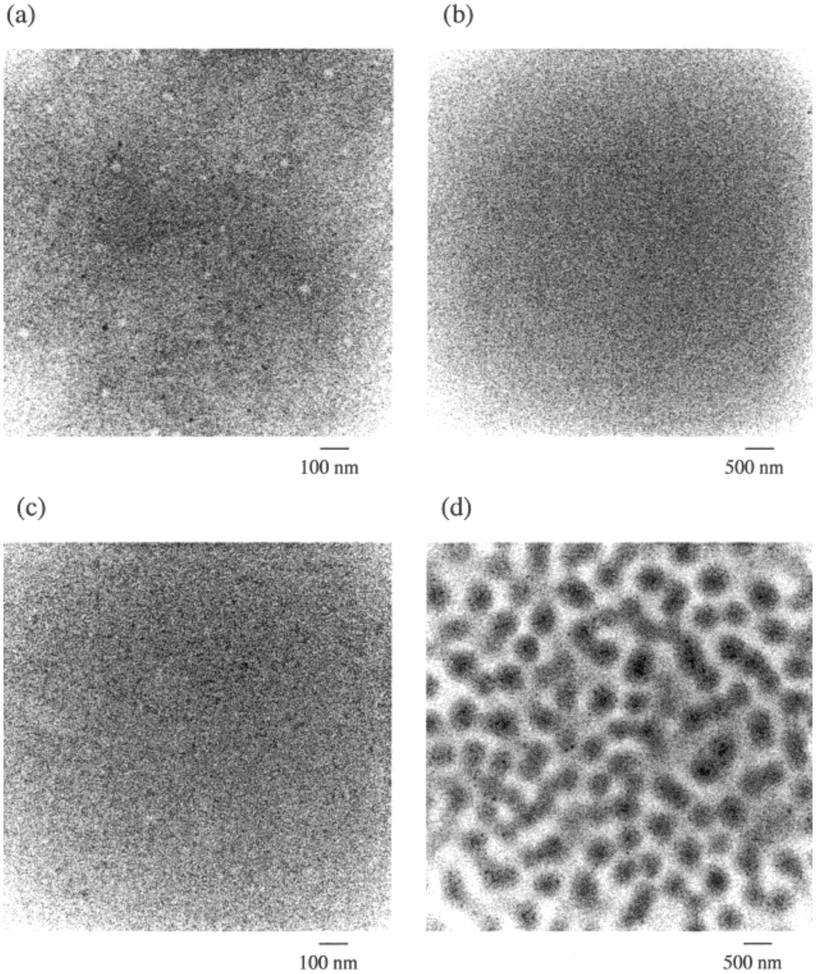

Figure 6. TEM pictures of (a) a random copolymer bulk film of poly(MMA/BzMA) (50/50), (b) PMMA homopolymer, (c) PBzMA homopolymer, and (d) a polymer blend of PMMA and PBzMA (1:1), with the magnifications of (a, c) 1.0×10^5 and (b, d) 2.0×10^4. Film thicknesses are ca. 100 nm.

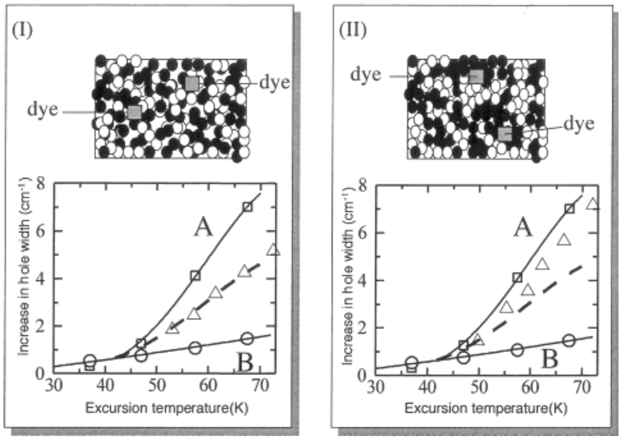

Figure 7. Schematic pictures of PHB measurements for (I) random copolymer films with randomly located comonomer units at nanoscopic level and for (II) random copolymer films with the existence of nanoscopic aggregation and preferential distribution of dye molecules into one of the nanodomains: (□) homopolymer A, (○) homopolymer B, (△) random copolymer, poly(A/B) (experimental), (- - -) hypothetical curve for case I.

1:1 and 3:1) even when they were annealed at 100 °C for 12 h. We can suppose that TPP is dissolved in PBzMA region easily compared to the PMMA region because TPP has a lot of phenyl units and PBzMA also has a phenyl unit. Any as-cast polymer blend samples of PMMA with PBzMA as well as random copolymer samples showed no microphase separation in the fluorescence micrographs. Thus, it can be expected that TPP is dissolved preferentially in the nanodomain of *n*-BMA or BzMA compared to the nanodomain of MMA in the present random copolymer films.

The random copolymers of poly(MMA/*n*-BMA) and poly(MMA/BzMA) showed single glass transition temperatures between T_g of PMMA (115 °C) and T_g of P(*n*-BMA) (24 °C) and between T_g of PMMA and T_g of PBzMA (61 °C), respectively.

Nanoscopic Aggregates in a Random Copolymer Bulk Film Studied with TEM. A transmission electron microscope (TEM) picture of 1.0×10^5 magnification for the random copolymer film of poly(MMA/BzMA) (50/50) dyed with RuO_4 for BzMA monomer units in Figure 6a shows bright-contrast domains with the diameter of 20−30 nm, suggesting the formation of MMA-rich nanoscopic aggregates in the random copolymer film. The fraction of the MMA-rich bright-contrast domains is rather small compared to the amount of MMA monomer units in the copolymer composition, which might be related to the amounts of blocklike distribution in monomer sequences of the random copolymer. Either PMMA or PBzMA homopolymer film showed no appreciable phase separation in their TEM pictures (Figure 6b,c), while their polymer blend with weight ratio of 1:1 (Figure 6d) showed clear phase separation with PBzMA-rich dark domains of ca. 500 nm diameter. The TEM picture for the random copolymer film of poly(MMA/BzMA) supports the above discussion on the PHB experiments, suggesting the formation of nanoscopic aggregates even in random copolymer bulk films of hydrophobic comonomers.

The difference in solubility parameters of monomer units which can be evaluated from cohesive energy densities of the monomers is often used as a measure of miscibility of polymer blends.[26] The solubility parameters for MMA and *n*-BMA are reported to be 9.3 and 8.7 $cal^{1/2}\ cm^{-3/2}$, respectively,[26] with an appropriate error range. The difference in solubility parameters for BzMA and MMA (0.04 $cal^{1/2}\ cm^{-3/2}$) is quite small compared to that for *n*-BMA and MMA (0.64 $cal^{1/2}\ cm^{-3/2}$).[27] This tendency has been ascertained by the above-mentioned observation of their polymer blends with a fluorescence optical microscope. It is noteworthy that even for the combination of BzMA and MMA which has no substantial difference in the solubility parameters and whose polymer blends and random copolymers look homogeneous with optical microscopic and DSC scale, their random copolymer bulk films are shown to include nanoscopic aggregation larger than 2.3 nm by PHB measurements and with 20−30 nm by TEM measurements.

Schematic pictures of PHB measurements for nanoscopic aggregation of random copolymer films are illustrated in Figure 7.

Conclusions

We studied the existence of nanoscopic aggregates in random copolymer films of MMA with *n*-BMA or BzMA by using photochemical hole burning (PHB) spectroscopy and TEM. The copolymers were polymerized with different comonomer ratios. The increase in hole widths at certain excursion temperatures in the copolymers of MMA with *n*-BMA is enhanced compared to that expected for the hypothetical system where MMA and *n*-BMA units are randomly dispersed. The results can be explained by nanoscopic aggregation of *n*-BMA units and its preferential inclusion of TPP. The increase in hole widths in the copolymers of MMA with BzMA is also enhanced compared to that expected for the corresponding hypothetical system, which suggests the nanoscopic aggregation of BzMA units in poly(MMA/BzMA) copolymer bulk films. The nanoscopic aggregation of MMA-rich phase in 20−30 nm scale in a random copolymer of poly(MMA/BzMA) was also ascertained by TEM with RuO_4 dyeing. The results were compared to the data of solubility parameters. PHB is proved to be an effective tool for studying the nanoscopic aggregation in transparent bulk films of random copolymer systems.

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