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Aggregation behavior of gel microspheres of it-poly(methyl methacrylate) from xylene solution

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Abstract

The aggregation behavior of gel microspheres of it-poly(methyl methacrylate) (it-PMMA) from xylene solution was studied using optical microscopy, electron microscopy, DSC and wide-angle X-ray diffractometry. When the dilute solution (0.05–2.0 wt%) of it-PMMA (M_n = 64 000, triad tacticity, 92% isotactic) was cooled to 25°C, the it-PMMA precipitated as swollen, crystalline gel-microspheres (G-MSs) with a diameter of about 1 μm, which stick together to form complex dendritic clusters. It has been found that the resulting clusters are well described as fractals. The fractal dimension of the aggregates is estimated to be about 1.5. On the other hand, when the rather concentrated solution (~2.0 wt%) was cooled to 10–15°C, G-MSs aggregate to form the porous, highly swollen gel. The process of aggregation of the G-MSs and the structures of gel of it-PMMA are important technologically and scientifically.

Keywords: it-poly(methyl methacrylate); Gel; Microsphere

1. Introduction

The crystal structure of isotactic poly(methyl methacrylate) (it-PMMA) has been studied in detail by some workers [1–5]. The double-stranded helix was finally proposed by Kusanagi et al. as the molecular structure of it-PMMA [4]. It seems interesting to study the crystallization behavior and supermolecular structure of this unique polymer. Recently, the crystallization behavior of it-PMMA with low molecular weights (it-PMMA oligomer) has been reported by Ute et al. [6]. It has been found that it-PMMA oligomers form a spherulitic structure. Thus far, the crystallization behavior of it-PMMA with high molecular weight from solution has not been reported, though the association of stereoregular poly(methyl methacrylates) has been studied by some workers [7–10].

The present investigation mainly deals with the crystallization-gelation behavior of it-PMMA from xylene solution. When the dilute xylene solution (0.05–0.50%) of it-PMMA was cooled to 25°C, it-PMMA precipitated as swollen, crystalline gel-microspheres (G-MSs) with a diameter of about 1 μm, which stick together to form complex random dendritic clusters. The clusters formed by the aggregation of G-MSs are characterized by their tenuous, chain-like structure. It has been found that the resulting clusters are well described as fractals. The fractal dimension, D, for the clusters was estimated using their optical micrographs to be $D = 1.50$. This work presents, to our knowledge, the first attempt to experimentally characterize the two-dimensional clusters of polymer microspheres using a visual technique. On the other hand, when the rather concentrated solution (2–20 wt%) was cooled to room temperature, G-MSs aggregated to form a porous, highly swollen gel. It was concluded that the diffusion-limited aggregation of G-MSs contributes to the formation of the porous structure. The process of aggregation of G-MSs and the structures of gel of it-PMMA are important technologically and scientifically.

2. Experimental

2.1. Materials

A sample of it-PMMA was kindly supplied by Mitsubishi

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Rayon, Ltd. The M_n, M_w/M_n, and triad tacticity of this it-PMMA are as follows:

Sample no.	M_n	M_w/M_n	rr(%): mr(%): mm (%)
it-PMMA	64 000	3.02	3.1: 3.9: 92.9

2.2. Sample preparation

Powders of it-PMMA were dissolved in xylene at 100°C to obtain 0.05–0.50 wt% solution (dilute solution) or 2–20 wt% solution (concentrated solution). Upon cooling the solution, aggregates of G-MSs settle slowly onto a glass slide or carbon-coated electron microscopic grids which are placed on the bottom of the vessel.

2.3. Measurements

Optical microscopy of the aggregates of G-MSs was performed with an Olympus optical microscope (NHSP-751P) equipped with an Olympus camera OM-N_2. The transmission electron microscopy (TEM) and scanning electron microscopy (SEM) were performed with a Nihon-Denshi model 2000 FXII and a Hitachi model S-2400, respectively.

Wide-angle X-ray diffraction (WAXD) patterns were obtained using a Toshiba X-ray generator (C-40H) equipped with a flat plate camera. Ni-filtered CuKα radiation was used as the X-ray source. Differential scanning calorimetry (DSC) was carried out over a temperature range from 20 to 180°C using a Perkin-Elmer DSC 7. Runs were conducted at a heating rate of 10°C/min.

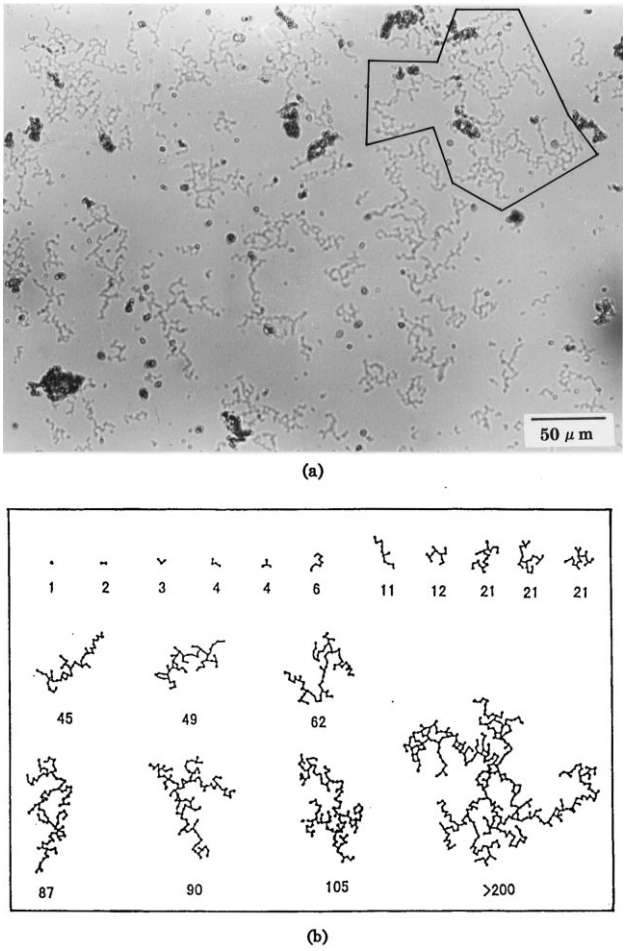

Fig. 1. An optical micrograph (a) and a corresponding scheme (b) of it-PMMA clusters precipitated from 0.10% xylene solution onto a glass slide at 25°C for 24 h. Gel microspheres stick together to form dendritic clusters.

3. Results and discussion

3.1. Aggregation of gel-microspheres of it-PMMA precipitated from dilute xylene solution

When the hot, dilute xylene solution of it-PMMA was maintained in a thermostat at 25°C, G-MSs were precipitation onto a glass slide placed on the bottom of the vessel. Optical micrographs of it-PMMA precipitated from 0.05, 0.10, and 0.50% xylene solutions were examined as a preliminary experiment. Well-developed clusters suitable for the study of the aggregation mechanism were formed from 0.05–0.10% xylene solution, whereas dense aggregates with complicated external shape were formed from 0.50% solution.

Fig. 1(a) is an optical micrograph of the clusters of G-MSs precipitated from 0.10% xylene solution onto a glass slide at 25°C for 24 h. As shown in Fig. 1(a), clusters containing a widely varying number of G-MSs coexist in the same sample. A cluster containing n particles is hereafter shown as 'cluster (n)'. Some representative clusters with different particle numbers are schematically shown in Fig. 1(b), where G-MSs are represented by solid circles having the same diameter. As shown in Fig. 1(a) and Fig.1(b), G-MSs are not dispersed randomly on a glass slide, but stick together to form complicated dendritic structures. These clusters of G-MSs exhibit the tenuous and ramified appearance characteristic of metal colloidal aggregates [11], metal electrodeposits [12,13], and soot [14].

As Fig. 1(a) and Fig. 1(b) reveal, one larger cluster is composed of some smaller clusters. For example, the largest clusters ($n > 200$) contain some smaller clusters ($n = 80$–100) which are composed of some even smaller clusters ($n = 40$–60), and so on. This seems to indicate that the it-PMMA clusters reveal self-assembling character which is characteristic of the fractal structure.

We will discuss the mechanism of cluster formation of it-PMMA from a single particle by introducing the concept of diffusion-limited aggregation. Since Witten and Sander developed a model for the diffusion-limited aggregation of particles [15], considerable theoretical and experimental studies have been carried out by many workers [11–18]. In the original Witten–Sander (WS) model, a cluster grows from a single immobile site, and only one particle is allowed to diffuse in the vicinity of the growing cluster

[15]. A fractal dimension for this WS model is estimated by computer simulation to be $D = 1.67$.

Kolb, Botet, and Jullian proposed a growth model (KBJ model) that describes the cluster–cluster aggregation [16]. According to their computer simulation, N_0 particles are initially randomly distributed on a periodic square lattice with L^2 sites. Brownian particles stick together upon contact to form clusters. The newly formed clusters can move randomly on the lattice, and they become larger and larger with the passage of time; clusters grow when they meet with other clusters. Finally, one large cluster is formed. A fractal dimension was estimated to be $D = 1.38$ for the low-density system [ρ_0 (N_0/L^2) = 0.06] [16].

It is interesting to note that the morphological features of it-PMMA clusters precipitated from dilute xylene solution are very similar to those formed by cluster–cluster aggregation [16], suggesting that the it-PMMA clusters grow during sedimentation onto the bottom of the vessel. However, the it-PMMA clusters are obviously different from the KBJ model in the following point. In the KBJ model, all particles are initially generated, and the clusters formed after a certain time interval contain a similar number of particles. On the other hand, as shown in Fig. 1, it-PMMA clusters with widely varying numbers of particles coexist.

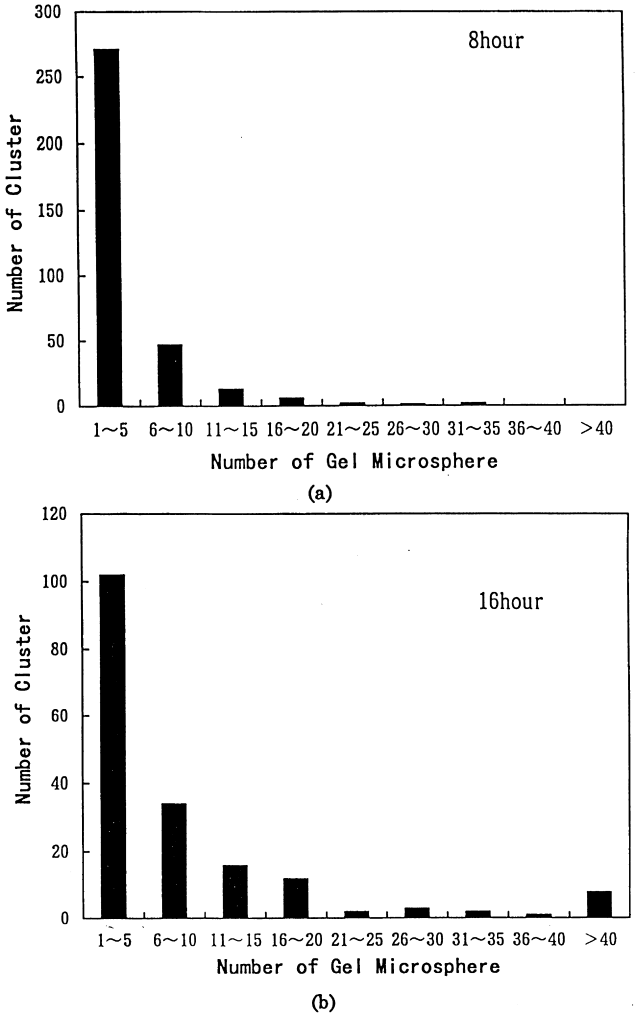

Fig. 2. Histograms showing the relation between the number of clusters containing n particles [$N_c(n)$] and n. Optical micrographs of it-PMMA clusters precipitated from 0.05% solution onto a glass slide at 25°C for 8 h (a) and 16 h (b) were used for the measurements.

In order to explain the above result, the following experiments were performed. The cluster size of it-PMMA precipitated from 0.05% xylene solution at 25°C was measured as a function of time (4, 8, 16, 24 h). The number of clusters containing n particles $N_c(n)$ was counted as a function of n. Only the $N_c(n) - n$ histograms for 8 and 16 h are shown in Fig. 2. As the histograms show, smaller clusters [$N_c(n < 5)$] were most frequently observed throughout the crystallization process (4–24 h) and the larger clusters [$N_c(n > 6)$] increase with time. These observations can be explained by assuming that the it-PMMA microspheres are generated with time in any position in the xylene solution. These considerations lead to the notion that the clusters grow during sedimentation onto the bottom of the vessel, i.e. large clusters are initially generated at an upper level of the vessel, whereas small clusters grow at a lower level of the vessel.

$N_c(n) - n$ histograms for 16 h are about the same as that for 24 h, indicating that the gelation-crystallization of it-PMMA from xylene solution at 25°C is accomplished after 16 h.

Precipitation of it-PMMA G-MSs from 0.10% xylene solution was also carried out in the narrow space between the two glass plates. Mica flakes, about 5 μm in thickness, were placed between the two glass plates as a spacer. It was observed that only small clusters ($n = 1$–5) were formed in the narrow space, indicating that the clusters grow during sedimentation onto the bottom of the vessel.

We tried to estimate a fractal dimension of the it-PMMA cluster precipitated from dilute xylene solution. The largest cluster in Fig. 1 is schematically shown in Fig. 3. The center of five concentric circles with a varying radius, R, is arbitrarily located near the center of gravity of the cluster. It was confirmed that the value of the fractal dimension is little affected by a slight shift of the center of concentric circles.

To obtain an estimate of a fractal dimension, the number of G-MSs, n, within each concentric circle with radius R is measured. The fractal dimension can be estimated using the following equation, where D represents a fractal dimension [19]:

$$n \propto R^D$$

Fig. 3 shows a logarithmic plot of n versus R. A fractal dimension for it-PMMA cluster precipitated from dilute xylene solution was estimated to be D~1.50.

As previously described, the fractal dimension, D, for the KBJ model (diffusion limited cluster–cluster aggregation) is 1.38, whereas D for the original WS model (diffusion limited aggregation of a single particle) is 1.68; cluster–cluster aggregation brings about the more ramified cluster having a smaller D.

Contrary to the WS and KBJ models, it-PMMA particles are successively generated in xylene solution with time, and consequently, single particle or small clusters coexist in the system throughout the gelation process. This may be why the *D* for it-PMMA is intermediate between those for the WS and KBJ models.

The above analysis is performed for a two-dimensional projection of the clusters of G-MSs which are originally three-dimensional in solution. Upon drying, the three-dimensional clusters in solution collapse to form two-dimensional structures. Weitz et al. studied the fractal structures formed by kinetic aggregation of aqueous gold colloids, making use of the fact that the fractal dimension remains unchanged upon projection, provided $D < 2$ [11]. This fact also supports the validity of our analytical technique (Fig. 3).

3.2. Morphology of it-PMMA gel formed from dilute xylene solution

Fig. 4(a) and Fig. 4(b) show TEM micrographs of it-PMMA precipitated from xylene solution onto the carbon coated electron microscopic grids. Flat, disk-like structures (D-structure) can be observed. It seems reasonable to assume that these D-structures originate from swollen, spherical G-MSs precipitated from xylene solution. Upon drying, the swollen G-MS collapse to form a nearly flat, D-structure. Arrows 1, 2, and 3 in Fig. 4(a) denote single, double and triple D-structures, respectively.

It is noteworthy that once plural D-structures collide with each other, they are merged and the boundary between them diminishes, indicating that G-MSs dispersed in solution are swollen with xylene, though the degree of swelling of G-MSs cannot at present be estimated.

Fig. 4(b) is another TEM micrograph of it-PMMA precipitated from xylene solution, showing complicated structures with an indefinite shape. These structures correspond to the immature clusters shown in Fig. 1. These observations demonstrate that many swollen G-MSs collide and are merged to form these structures. Dotted circles in Fig. 4(b) denote an original single G-MS.

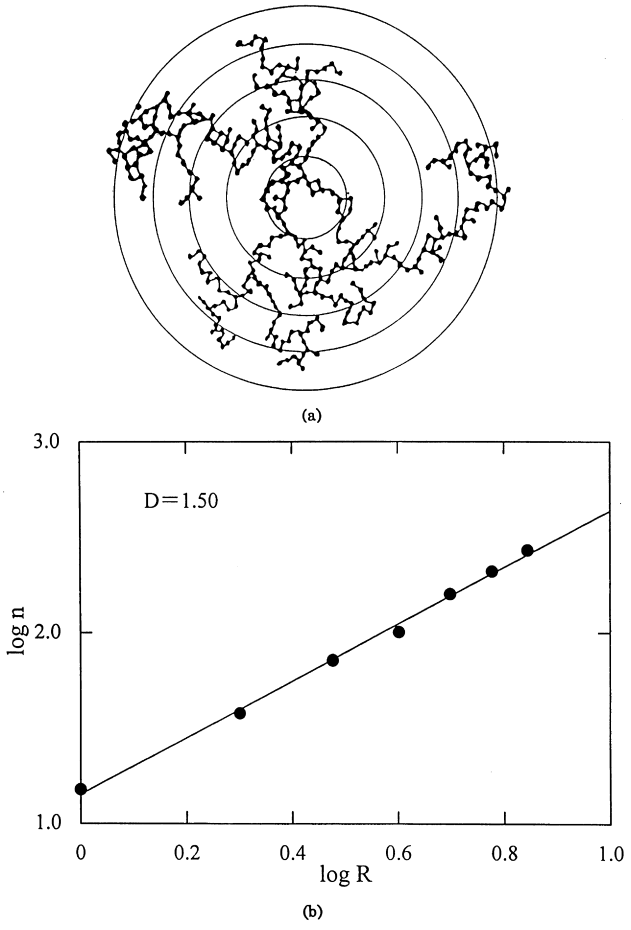

Fig. 3. (a) Schematic representation of the largest cluster in Fig. 1 and five concentric circles with varying radius, *R*. (b) A log *N* (number of particles in each concentric circle)–log *R* plot for the determination of a fractal dimension of the it-PMMA cluster.

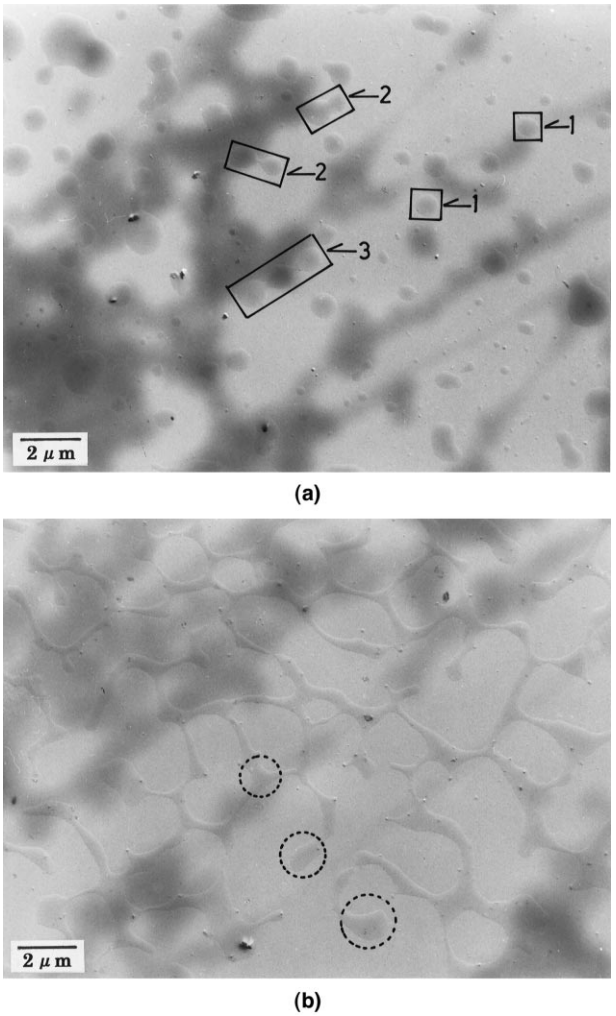

Fig. 4. Transmission electron micrographs of it-PMMA gel microspheres (a) and clusters (b) precipitated from 0.10% xylene solution onto carbon-coated electron miscroscopic grids at 25°C. Arrows 1, 2, and 3 in (a) denote single, double, and triple gel particles and dotted circles in (b) denote an original gel microsphere.

Fig. 5(a) is a schematic representation of a swollen G-MS, demonstrating the network structure composed of fine crystallites, amorphous molecules, and xylene. The fine crystallites with double-stranded molecules behave as a knot of the swollen gel. The scheme in Fig. 5(b) reveals that two G-MSs are merged and the boundary between them diminishes. If many G-MSs are merged after fractal aggregation, complicated structures such as those shown in Fig. 4(b) are formed.

Our discussions in the previous sections concentrate on the aggregation behaviour of G-MSs. The formation mechanism of a G-MS is not yet clear. Two probable mechanisms can be assumed for the crystallization-phase separation behavior of a G-MS:

1. fine crystallites of it-PMMA first separate out from xylene solution and then aggregate to form a swollen gel particle (G-MS);
2. spherical, it-PMMA rich liquid phases are first phase-separated out from xylene solution and then it-PMMA crystallizes in them.In both cases, G-MS which have grown to about 1 μm begin to settle to the bottom of the vessel, overcoming the Brownian motion.

Recently, thermoreversible gelation of syndiotactic PMMA (st-PMMA) has been studied in detail by Berghmans et al. using different experimental techniques [20]. They proposed that a fast intramolecular change from a coil to a helix conformation is followed by a slower intermolecular association, leading to the formation of the gel network, or at low concentration, to the formation of micro gel particle [20]. In view of the gelation behavior of st-PMMA, mechanism (A) is a plausible one for the gelation of it-PMMA. Although we do not have conclusive proof for this mechanism, it seems reasonable to assume that the crystallization of it-PMMA is due to coil-to-double-stranded helix transition followed by an intermolecular association, as is the case of st-PMMA. Further studies are now in progress.

3.3. Morphology of it-PMMA gel formed from concentrated xylene solution

When concentrated xylene solution (2–20 wt%) of it-PMMA was cooled to 25°C, an elastic, semi-transparent, and highly swollen gel (S-GEL) was formed at the bottom of the vessel. The degree of swelling of as-prepared S-GEL is dependent on the concentration of the xylene solution: as-prepared S-GELs formed from 2–5, 10, and 20% xylene solutions contain about 350, 210, and 160% of xylene, respectively. It seems reasonable to assume that G-MSs aggregate to form the more dense network from the more

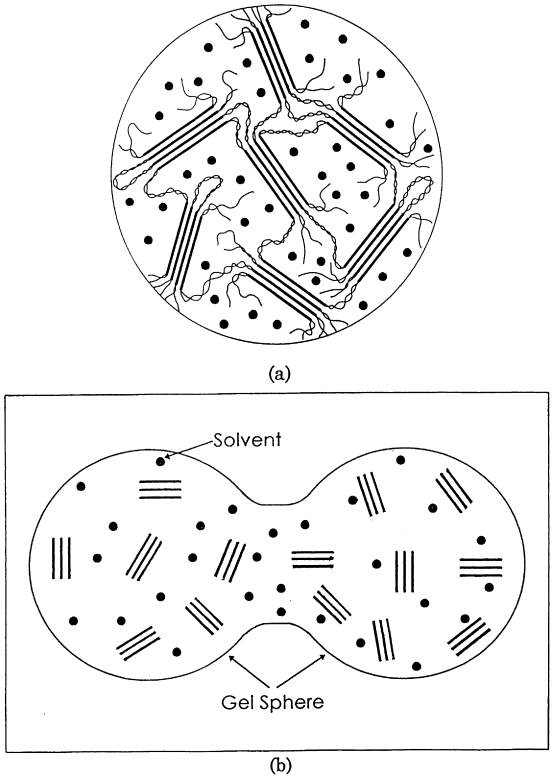

Fig. 5. Schematic representation of a swollen gel microsphere (G-MS) of it-PMMA (a) and two merged G-MSs (b).

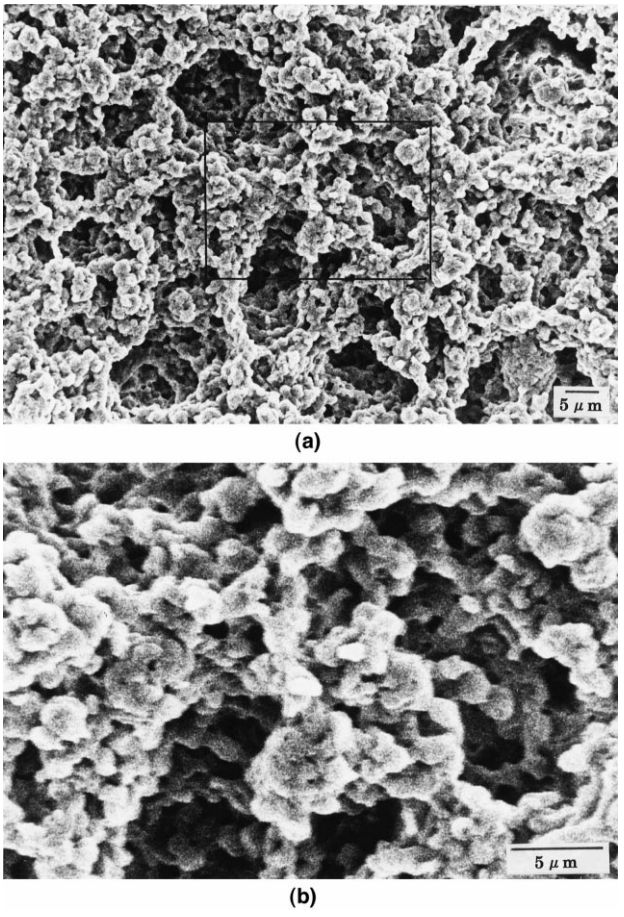

Fig. 6. Scanning electron micrographs of it-PMMA gel grown from 20 wt% xylene solution. (b) Enlarged detail of a part of (a).

concentrated xylene solution. S-GEL loses its transparency when xylene is pressed out.

Fig. 6 is a SEM micrograph of the dried gel of it-PMMA (D-GEL) formed from 20% xylene solution, showing that the fine G-MSs with a diameter of about 1 μm stick together to form the three-dimensional network structure. D-GEL is characterized by its porous structure: many voids with varying diameters are visible in Fig. 6. The maximum diameter of the voids is as large as about 10 μm. This is the main reason why S-GEL can contain much solvent. It seems reasonable to conclude that the diffusion-limited aggregation of G-MSs contributes to the formation of the porous structure, although the fractical dimension cannot be estimated.

3.4. Thermal behavior of it-PMMA

The thermal behavior of it-PMMA was studied using DSC. Fig. 7 shows DSC thermograms for the heating of D-GELs formed from 2–20 wt% xylene solution at 25°C, exhibiting two thermal events, a glass transition (T_g) at about 40°C and a melting endotherm at about 140°C. T_g was determined as schematically shown in the upper-left corner of Fig. 7. In this case, the unusual endothermic peak appearing near the final stage of the glass transition hinders the exact evaluation of T_g.

Ute et al. studied the T_g of uniform it-PMMA from 13mer to 50mer; the T_g of it-PMMA with infinite molecular weight is estimated to be 49.6°C [6]. As Fig. 7 shows, the T_g of D-GEL is lower than the Tg of it-PMMA with infinite molecular weight. This discrepancy is due to the broader molecular weight distribution and lower tacticity of the it-PMMA used in this study.

A crystallization exotherm is no longer observed in Fig. 7, indicating that the crystallization of it-PMMA is already finished during gelation. Ute reported the equilibrium melting point of it-PMMA ($T_{m\infty}$: melting point of extended-chain crystals with infinite molecular weight) to be 171.1°C using the T_m–DP^{-1} plot of uniform it-PMMA with varying molecular weights [6]. The melting point of D-GEL, 140.6°C, is appreciably lower than the $T_{m\infty}$ of it-PMMA, indicating that D-GEL is composed of fine, imperfect crystallites.

The ΔH (observed heat of fusion per repeating unit) to ΔH_u (heat of fusion per repeating unit) ratio provides the crystallinity. ΔH of D-GEL was estimated from the area of the melting peak, whereas ΔH_u was estimated by Kusy to be 1200 ± 80 cal mol^{-1} [21]. The crystallinity of D-GEL is estimated to be 0.30, being as low as that of wholly aromatic, thermoplastic polymers.

A possible reason for the low crystallinity of the solution-grown gel of it-PMMA is as follows. The transition of it-PMMA molecules from coil to double-stranded helix must be accomplished before they are introduced into the crystal. If the plural segments in an individual molecule begin to take part in the double-stranded helix, as shown in Fig. 5(a), it seems reasonable to assume that the crystal growth is restricted to a certain extent, at least, in the longitudinal direction.

3.5. Wide-angle X-ray studies of the it-PMMA precipitated from xylene solution

The crystal structure of it-PMMA gel precipitated from 2% xylene solution at 25°C for 24 h has been studied. For WAXD studies of S-GEL, as-precipitated swollen gel was wrapped with aluminum foil to prevent solvent evaporation. WAXD patterns for S-GEL and D-GEL are shown in Fig. 8(a) and Fig. 8(b), respectively. Many radial streaks due to aluminum and a diffuse halo due to xylene ($2\theta = 20$) are superimposed on the diffraction rings. Both S-GEL and D-GEL produce some clear diffraction rings of the WAXD patterns. Main diffraction peaks in these WAXD patterns can be assigned on the basis of the crystal structure proposed by Kusanagi et al. [4], indicating that D-GEL and S-GEL have the same crystal structure. These results lead to

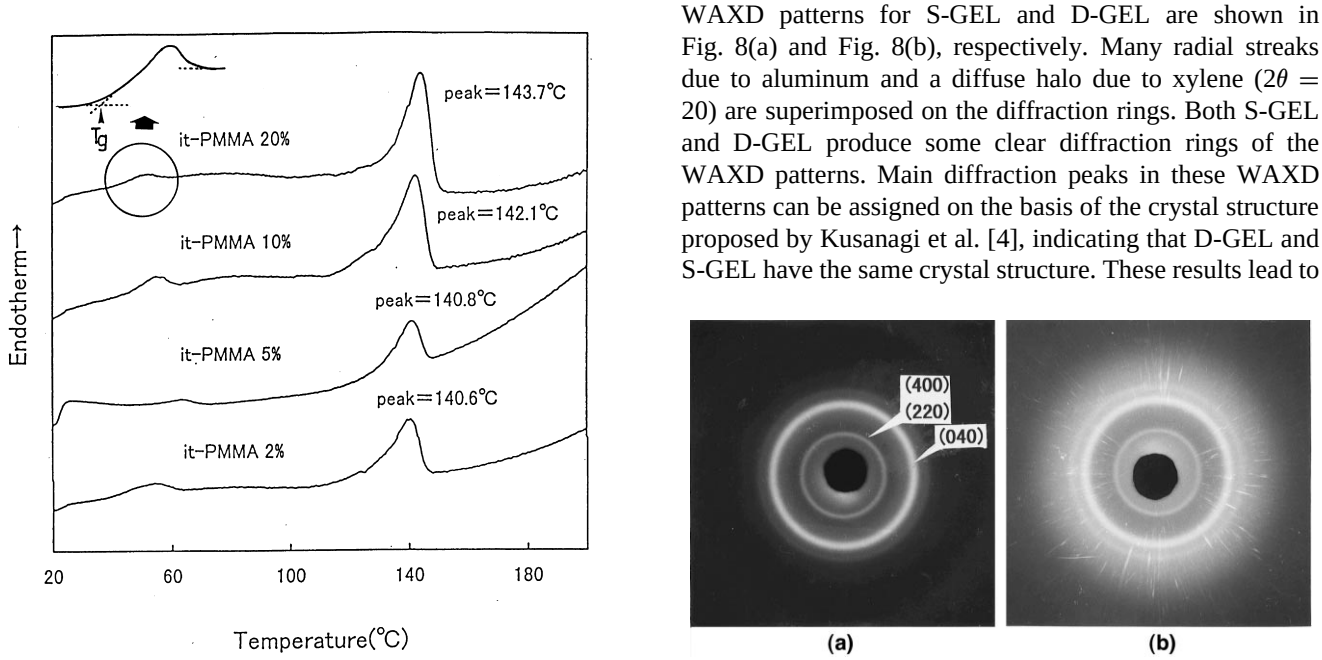

Fig. 7. DSC thermograms of the dried gels of it-PMMA formed from 2–20% xylene solution at 25°C.

Fig. 8. Wide-angle X-ray diffraction patterns of it-PMMA gel precipitated from 20 wt% xylene solution. (a) As-grown, swollen gel. (b) Dried gel.

the conclusion that crystal solvate is not formed during the crystallization-gelation of it-PMMA from xylene solution.

4. Conclusions

The crystallization-gelation behavior of it-PMMA with a molecular weight of 64 000 from xylene solution has been studied. When the hot, dilute solution of it-PMMA is cooled to 25°C, it-PMMA is phase separated as swollen, crystalline gel particles, which stick together to form complicated dendritic clusters. The morphological features of the clusters of it-PMMA are very similar to those of the fractal structure formed by the diffusion-limited cluster–cluster aggregation. The fractal dimension of the well-developed it-PMMA cluster was estimated to be 1.50. On the other hand, when the concentrated solution ($>$ 2%) was cooled to 25°C, the gel particles aggregate to form a porous, highly swollen gel.

DSC thermograms exhibit two thermal events, T_g at about 40°C and melting exotherm at 140°C. The crystallinity of it-PMMA gel is estimated to be 0.30. It has been confirmed by WAXD studies that it-PMMA–xylene crystal solvate is not formed during crystallization-gelation from xylene solution.

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