

Dynamic light scattering studies on poly(vinyl chloride) clusters and aggregates in tetrahydrofuran

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Abstract

A novel method to characterize the history of processing for poly(vinyl chloride) (PVC) has been presented. This method consists of: (1) dissolving PVC in tetrahydrofuran; followed by (2) dynamic light scattering (DLS); and (3) cluster-size distribution analysis. It was found that the characteristic decay time distribution function $G(\tau)$ showed the history of sample treatment, where τ is the characteristic decay time. In the case of dilute solutions of virgin PVC resin, $G(\tau)$ was dominated by the fast mode at $\tau_f \approx 30 \mu\text{s}$. This is the first observation of the presence of PVC clusters of ca. 4.5–6.0 nm. On the other hand, those prepared from a milled PVC film exhibited another peak at a larger characteristic time, $\tau_s \approx 3 \text{ ms}$. This indicates that aggregates about 100 times larger than the clusters are formed during processing. The formation of the larger clusters was also verified by atomic force microscopy. It is concluded that DLS is a sensitive means in characterizing gel structure and processing history for PVC films. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Poly(vinyl chloride); Dynamic light scattering; Aggregation process

1. Introduction

It has been already passed more than 60 years since poly(vinyl chloride) (PVC) was commercialized in 1926 by Waldo Semon [1]. In spite of its wide range of application not only in the industry but also in daily life, the relationship between the structure and properties of PVC has not been well elucidated compared with other commercial polymers, such as polyethylene, polypropylene, and poly(vinyl alcohol). This is mainly due to the presence of hierarchical structures. That is, PVC resins consist of primary particles with a micrometer order. The primary particle plays as a unit of flow in the molten state. An aggregate of primary particles becomes a stable particle called grain whose size is on sub-millimeters. On the other hand, the primary particles themselves are formed with smaller particles called domains of submicrometer order or with much smaller particles called microdomains of 10 nm order [2,3]. The hierarchical structure also makes PVC possible for a gel-like behavior during processing.

Recently, much attention has been refocused on the sol-gel transition of PVC. For example, the rheological proper-

ties of PVC resin solutions were extensively investigated by Aoki et al. [4–8]. They observed a power-law behavior in the storage (G') and loss moduli (G'') of PVC in dioctyl phthalate solutions as a function of angular frequency (ω), i.e. $G' = G'' \sim \omega^n$, where n is an exponent. It is known that this power law-behavior appears at the sol-gel transition [9,10]. Guenet and coworkers investigated the gel structure of PVC in di- and mono-esters by static light scattering and discussed on the basis of fractal analysis [11]. They observed the presence of fibrillar structure with the fractal dimension of 1.5 independent of solvent type.

Compared to the investigations of gel structures in several solvents as demonstrated above, studies on structure and properties of bulk PVC have been limited to qualitative discussions because of difficulty in its characterization as is described in the book by Guenet [12] and in the review by te Nijenhuis [13]. This is again partially due to the hierarchical structure of PVC. Determination of the degree of gelation for PVC is one of the most important issues in PVC industries. In other words, characterization of gelation (often called “fusion”) is an essential problem that has not been properly addressed. Although several methods, i.e.: (1) capillary rheometry [14]; (2) methylene chloride method (measurement of the degree of swelling after immersing in methylene chloride); and (3) thermal analysis [15], have been proposed, neither of them is decisive. The capillary rheometry merely provides information about

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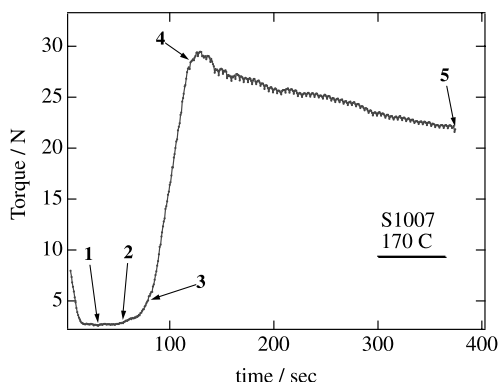


Fig. 1. Time-variation of torque during milling process of PVC resins at 170°C.

melting behavior and is nothing to do with fusion (gelation) of PVC. The methylene chloride method reflects only the surface properties of molded PVCs or films. The thermal analysis is useful to detect the melting behavior of PVC crystallites. However, the information is not correlated with fusion of grains, i.e. gelation.

In this paper, we propose a novel method to characterize the structure of PVC films made by roll-milling. This method includes dissolution of PVC films with tetrahydrofuran (THF), followed by dynamic light scattering (DLS) analyses on the solution. The presence of PVC clusters smaller than microdomains was observed for the first time by DLS and was verified by atomic force microscopy. It will be demonstrated that the DLS correlogram clearly exhibits the history of processing done on PVC resins.

2. Experimental section

2.1. Samples

Commercial grade poly(vinyl chloride) (PVC) resins, S1007, Kaneka, Co. Ltd., were employed without further purification. The degree of polymerization, P , was determined to be 680 by inherent viscosity measurement according to JIS 6721 (an equivalent standard to ASTM D1243). The polydispersity index, i.e. the ratio of the weight and number average molecular weights, was estimated to be 1.9 by gel permeation chromatography (GPC). The triad microstructure of the resin was, iso = 8.8, syndio = 52.2, and hetero = 39%. PVC sheets were prepared from the resins by using a Labo Plastomill, Toyo Seiki, Co. Ltd, Tokyo, Japan. PVC resin (46 g) was loaded in the chamber. The resin was preheated for 2 min up to 170°C and then the mill was started to rotate at a rate of 30.0 rpm. Fig. 1 shows the variation of torque generated by milling of PVC resins at 170°C. As indicated by the numbers, the milling process could be classified to five stages according to the change of torque. In the stages 1 and 2, PVC resins melt by heating, resulting in a decrease in viscosity. This is the reason why

the torque is very low in these stages. However, the torque increases steeply at ca. 80 s. (stage 3) due to ‘fusion’ of PVC resin (or in another word, gelation). Note that, in general, heating, resulting in a decrease in torque reduces the viscosity of most polymers. Therefore, this type of torque change during processing is rather unique in PVC. On the basis of this torque behavior of PVC processing, five PVC samples corresponding to these stages were obtained. Then, these PVC samples, including the virgin PVC (PVC resin; S1007-0) as well as milled PVC film (S1007-5), were dissolved in THF with stirring at room temperature. After filtering with a 0.25 μm filter, the THF solution was examined by dynamic light scattering (DLS). The concentration of PVC in THF was 2 wt%.

2.2. DLS

DLS measurements were carried out on a DLS/SLS-5000, ALV, Langen, Germany, with a 22 mW He–Ne laser (Uniphase, USA). A use of static and dynamic enhancers and a high quantum efficient (HQ) avalanche photo diode detection system (ALV) led to an increase of photon counting rate by a factor of more than 50 times compared to a conventional system with pinholes and a photomultiplier. All of the DLS measurements were conducted at $T_{\text{obs}} = 20^\circ\text{C}$ and at the scattering angle of 90° . The characteristic decay time distribution function, $G(\tau)$, was obtained from $g^{(2)}(t)$ with an inverse Laplace transform program (a constrained regularization program, CONTIN), where t and τ are the time interval between two-successive photon countings and the characteristic decay time, respectively. The details of the data analysis are discussed elsewhere [16].

2.3. Atomic force microscopy

Atomic force microscopy (AFM) was carried out with a NanoScope IIIa, Digital Instruments, TX. A $3.54 \times 10^{-6} \text{ g/cm}^3$ of PVC solution in tetrahydrofuran (THF) was

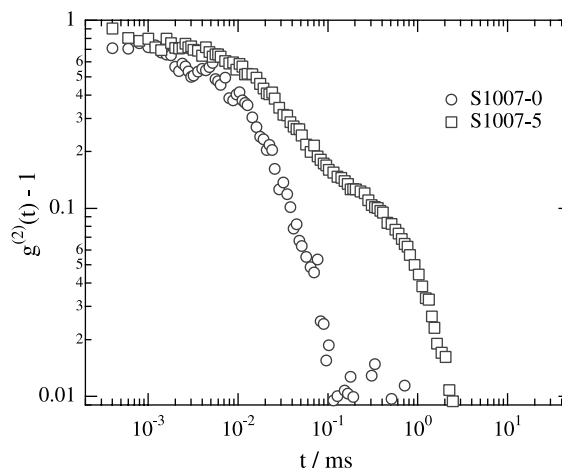


Fig. 2. Double logarithmic plots of the intensity time correlation functions (ICF) for THF solutions of virgin PVC resin (circles; S1007-0) and milled PVC film (squares; S1007-5).

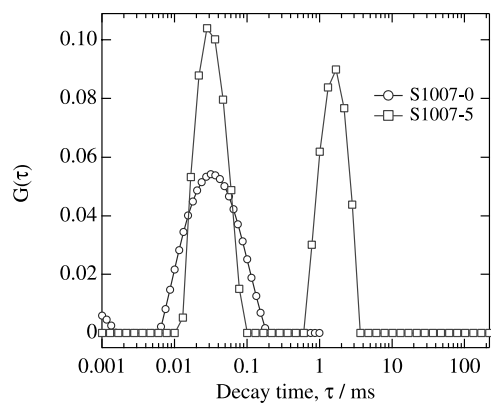


Fig. 3. Relaxation distribution functions, $G(\tau)$, for THF solutions of S1007-0 (circles) and S1007-5 (squares).

cast on a mica substrate. After evaporation of THF, the sample was examined with the microscope in the tapping mode at room temperature.

3. Results and discussion

3.1. Comparison of PVC resin and milled PVC

Fig. 2 shows double logarithmic plots of the intensity correlation function (ICF), $g^{(2)}(t) - 1$, for S1007-0 (virgin resin) and S1007-5 (milled PVC). The virgin resin seems to have a single decay around $t \approx 0.03$ ms, while the milled PVC has two relaxation modes at $t \approx 0.03$ ms and 1 ms. The presence of these relaxation modes is more clearly displayed by taking inverse Laplace transform of ICF using constrained regularization program, CONTIN [16], as follows,

$$g^{(2)}(t) - 1 = \left[\int_0^\infty G(\tau) \exp(-t/\tau) d\tau^{-1} \right]^2 \quad (1)$$

Fig. 3 shows the decay time distribution function, $G(\tau)$, for the virgin PVC (S1007-0) and milled PVC (S1007-5). Here, the former exhibits a unimodal distribution, while the latter indicates a bimodal distribution. The peak in $G(\tau)$ for S1007-0, i.e. the first mode, corresponds to the translational diffusion of the smallest unit of PVC clusters. The apparent hydrodynamic radius of the PVC clusters, $R_{a,f}$, can be estimated via the Stokes–Einstein equation, i.e.

$$R_{a,f} = \frac{kT}{6\pi\eta} q^2 \tau_f \quad (2)$$

Here, kT is the Boltzmann energy, η is the solvent viscosity ($\eta = 0.487$ cP for THF at 20°C), q is the scattering vector ($\equiv 4\pi \sin \lambda/\eta$; the refractive index $n = 1.409$ for THF, $\theta = 90^\circ$ and $\lambda = 632.8$ nm). The size of this unit-cluster, $R_{a,f}$, is evaluated to be $R_{a,f} = 5.5$ nm. The radius of gyration of the PVC chain with $P = 680$ in unperturbed state is estimated to be around 6.0 nm by employing the value of the characteristic ratio $C_\infty = 6.70$ [17]. Hence, these unit-clusters may be

assigned to molecularly dispersed PVC chains in THF. $G(\tau)$ for the milled PVC, on the other hand, indicates the presence of the slow mode assigned to the translational diffusion of aggregates formed during processing. The size of the aggregates, $R_{a,s}$, was estimated with Eq. 2 by replacing τ_f by τ_s . The typical values of $R_{a,s}$ are 200 nm, and are about 60 times larger than those in the virgin resin. This observation is quite interesting since the history of processing is memorized as the cluster size. If the solvent, i.e. THF, dissolves PVC completely, $G(\tau)$ for the milled PVC should be the same as that for the virgin PVC. On the other hand, if degradation takes place during the process, the corresponding $G(\tau)$ would have a peak at a smaller τ but not at the larger τ . Therefore, it can be deduced that the appearance of the slow mode indicates formation of larger clusters by processing and the clusters are stable enough to resist against dissolution by THF. From this aspect, THF should be regarded as a dispersant rather than a solvent for PVC resin.

In order to confirm the formation of these stable clusters, an AFM observation was carried out on both virgin and milled PVCs. Fig. 4 shows the results of AFM. As shown in Fig. 4a, small dots (i.e. clusters) with 20 nm large are dispersed. Such dots were observed everywhere on the mica. The estimated size is a few times larger than that obtained by DLS. Hence, it is deduced that these dots correspond to small clusters made of a few PVC chains each. On the other hand, as shown in Fig. 4b, the AFM image for milled PVC shows the presence of both small and large clusters. The diameters of these clusters are estimated to be about 20 and 420 nm, respectively, from the half-width of the cross-sectional plot along the dashed line indicated in Fig. 4c. Again, such a view was observed everywhere on the mica. Hence, we conclude that these two types of clusters correspond to the primary clusters ((a) small aggregates comprising a few PVC chains; and (b) and the large aggregates).

3.2. Growth of aggregates by roll-mill processing

Fig. 5 shows changes of $G(\tau)$ s taken at the different stages of processing. Similar to Fig. 3, a double mode distribution of clusters is clearly found in all stages except for the virgin PVC (open circles). As processing goes on, the slow mode appears and its position shifts progressively to the larger decay time side.

Fig. 6 shows the corresponding AFM pictures in stages 1–4. In stages 1 and 2, small clusters with 10–20 nm large are scattered. On the other hand, huge clusters, i.e. aggregates, are present in the stages 3 and 4 in addition to the small clusters. The height of these clusters was also estimated to be a few nanometers for the small clusters and 90 nm for the aggregates. Therefore, the shapes of both particles are more or less flattened during evaporation process.

Fig. 7 shows the variation of PVC clusters as well as the

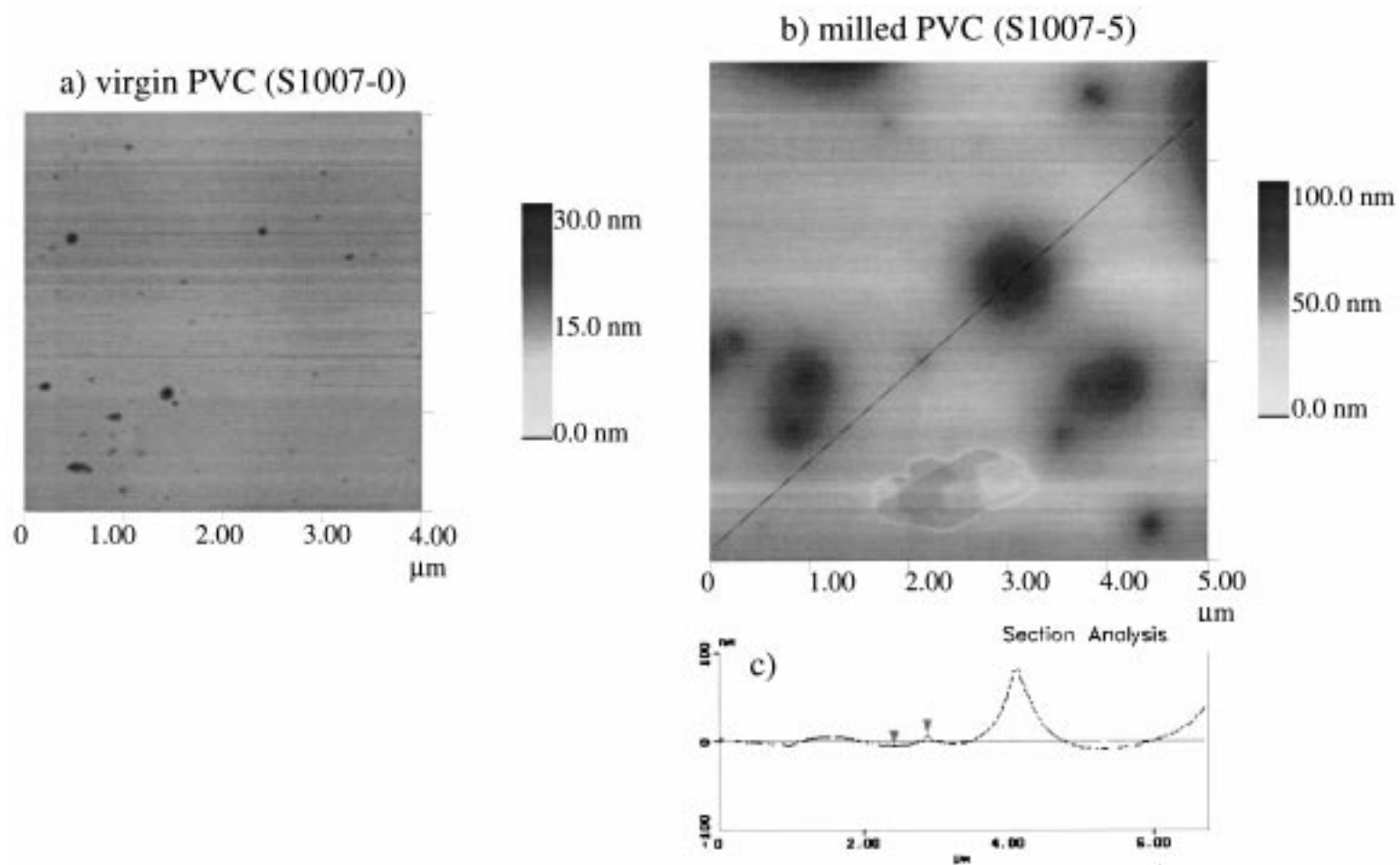


Fig. 4. AFM images for (a) virgin PVC (S1007-0) and (b) milled PVC resin (S1007-5), (c) the height distribution of the milled PVC resin (S1007-5) along the line in (b). Dots in the top figure correspond to the virgin PVC clusters whose radius is ca. 20 nm. On the other hand, two types of clusters with 20 and 420 nm in radius are seen in the solution cast PVC prepared from milled PVC.

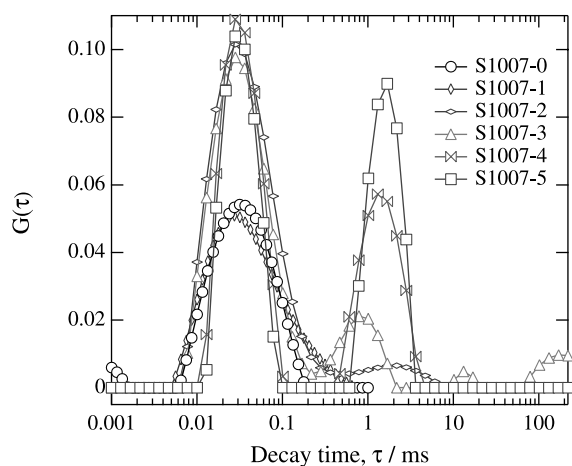


Fig. 5. Variation of $G(\tau)$ for PVCs sampled at different stages of milling process.

torque change during processing at 170°C evaluated by DLS ($R_{a,f}$ and $R_{a,s}$) and by AFM (R_{small} and R_{large}). In the beginning of processing, i.e. for the low torque region ($t < 100$ s), $R_{a,f}$ and R_{small} are about 5 and 20 nm, respectively. The discrepancy in the size observed by the two methods may be

attributed to the following reason. The PVC chains are coagulated to each other to form small clusters during evaporation process of the dispersant and are flattened on the mica substrate. In accordance to the abrupt increase in the torque at $t \approx 100$ s, aggregation takes place, which is detected as a drastic change in the characteristic size of the system, i.e. $R_{a,s}$ and R_{large} . In the late stage ($t > 200$ s), large clusters of the order of a few hundred nanometers appear as a result of gelation of PVC by processing. Though the size of particles evaluated by AFM is larger than that of DLS, this is due to the lack of statistics in the observation of AFM. Hence, the agreement of the larger cluster size evaluated by the two methods is again satisfactory.

3.3. Stability of the aggregates

Finally, we examined the stability of the large clusters against mechanical agitation. The milled PVC solutions in a test tube were ultrasonicated for given periods of time and re-examined with DLS as a function of the exposure time, t_{exp} . An ultrasonic cleaner (Bransonic, Model B1200, Emerson-Japan) was used for ultrasonication. The power and frequency were 60 W and 47 kHz, respectively. Fig. 8

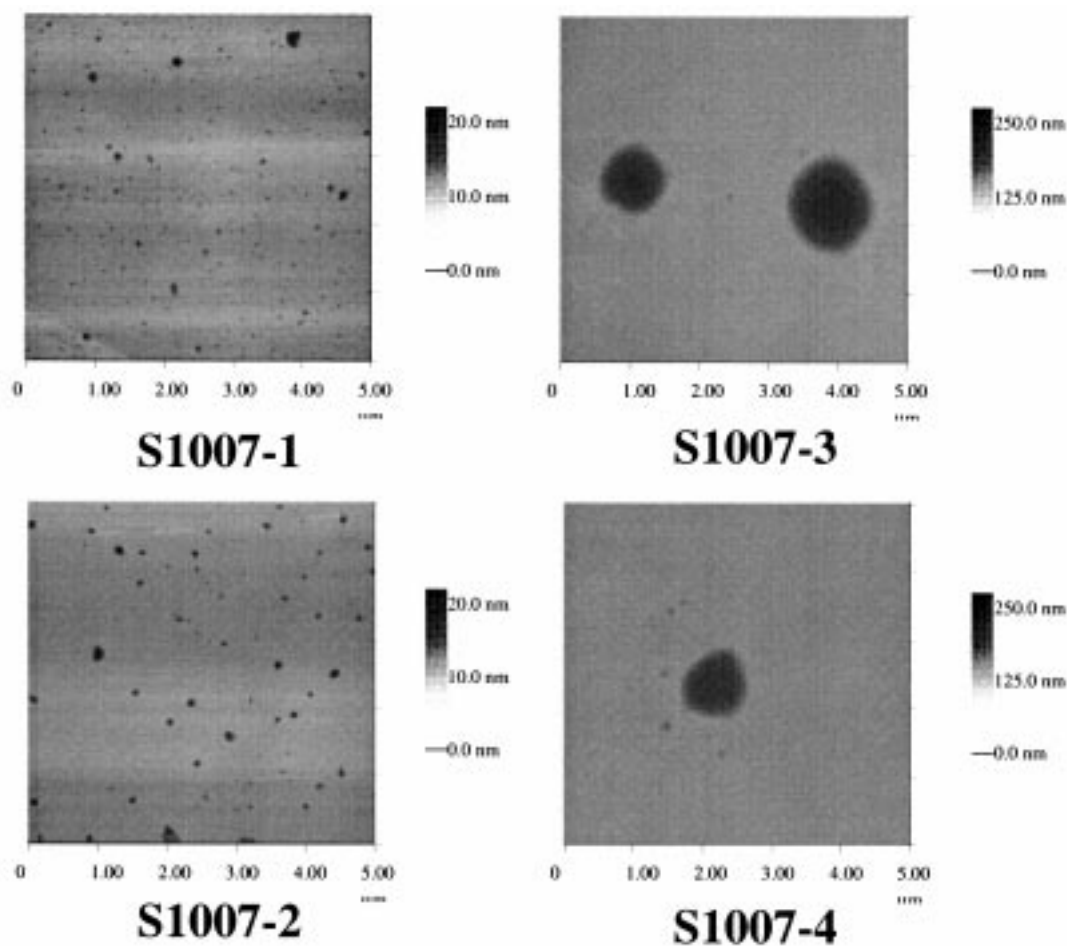


Fig. 6. AFM images for PVCs sampled at different stages of milling process. In stages 1 and 2, only small clusters of about 30 nm large are observed. On the other hand, aggregates of a few hundred nanometers large are observed in addition to small clusters in stages 3 and 4.

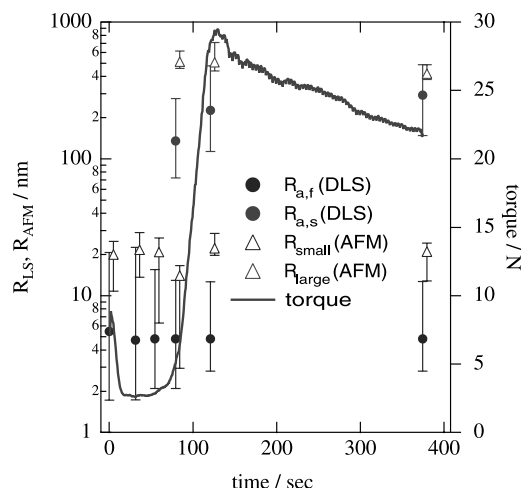


Fig. 7. Changes of the cluster and aggregate sizes and torque as a function of mill-processing time. A comparison of the cluster and aggregate sizes obtained by DLS and AFM is also made.

shows the cluster distribution functions of milled PVC film obtained after ultrasonication for $t_{\text{exp}} = 0, 10, 20, 35, 45, 55$ min. The temperature of the sample was maintained to be around 20°C by adding ice cubes to the water bath so as to avoid temperature elevation by ultrasonication. As shown in the figure, the slow mode indicating the large clusters does not disappear by the exposure of ultrasonic wave even for $t_{\text{exp}} = 55$ min. In order to analyze the t_{exp} dependence of $G(\tau)$, the area ratio of the peaks of the fast and slow modes is plotted in Fig. 9. This ratio is a measure of the population of the aggregates with respect to that of the virgin particles. As shown in the figure, the ratio is invariant against t_{exp} . Therefore, it may be concluded that the large clusters are quite stable against the solvent (THF) and mechanical vibration.

The feasibility of DLS for investigation of the cluster and aggregate structures of PVC resins can be extended to the analysis of gelation of PVC, which takes place during processing. It should be noted here that studies on gelation

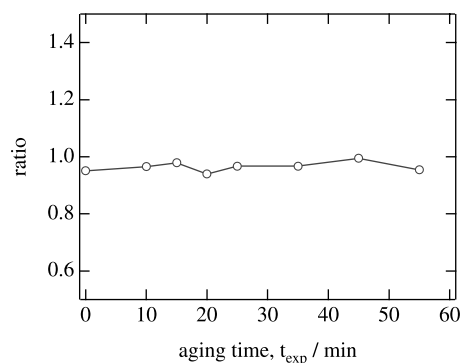


Fig. 9. Exposure-time dependence of the area ratio of the peaks of the fast and slow modes in $G(\tau)$.

of PVC have been carried out mostly by focusing on degradation process of PVC particles. The method proposed here, on the other hand, clarifies the gelation process by visualizing cluster evolution from the small clusters of nanometer order to integrated structures of submicrometer order. Furthermore, this method can be used to trace the history of processing by simply measuring the cluster distribution of PVC in THF. Similar results were obtained for PVC resins having different degrees of polymerization (460–1650). It should be also mentioned that the aggregate size has a tendency to increase by increasing the processing temperature.

4. Conclusions

Cluster structures of virgin and milled PVC resins were investigated by DLS. The resins were dispersed in THF and the size of clusters was estimated by DLS. It was found that the virgin PVC resins can be molecularly dispersed in THF and the size was estimated to be ca. 5 nm. By roll-milling at 170°C , the PVC clusters form aggregated structures whose sizes are 300–600 nm. The presence of the two types of clusters was verified by AFM. The formation of these

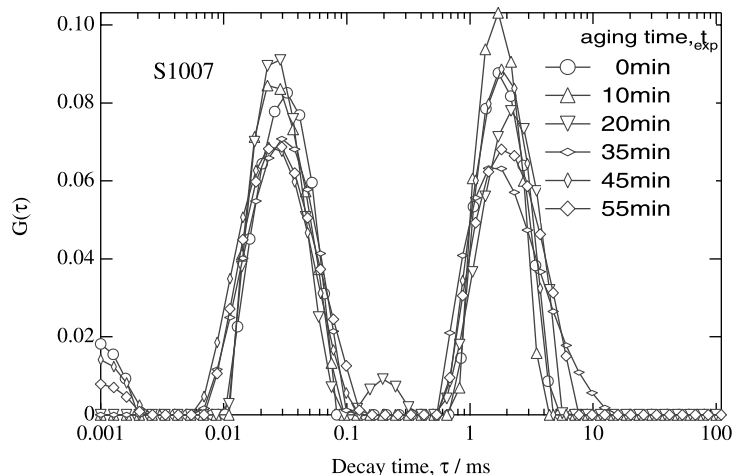


Fig. 8. Variation of $G(\tau)$ for solutions of milled PVC resins exposed by ultrasonication for different exposure times, t_{exp} .

aggregates was found to be in correlation with the rapid increase in the viscosity during milling process. It was also found that these cluster structures are quite stable against its solvent, i.e. THF.

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