

# Swelling of PVC Particles during Gelation and Fusion of Plastisols as Observed with Small-Angle Light Scattering\*

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## Synopsis

Small-angle light scattering was employed as a nondestructive technique for the *in situ* observation of swelling of PVC particles during gelation and fusion. One typical plastisol grade of PVC and three different plasticizers were used. The results demonstrate that quantitative measurements of average PVC particle size appear possible while they are in the process of swelling with plasticizers. From the degree of swelling the solvent power of plasticizers may be evaluated. The ranking of plasticizers made in this manner was in good agreement with the previous studies involving viscoelastic measurements.

## INTRODUCTION

PVC plastisol is dispersion of PVC particles in a plasticizer at approximately 50% volume concentration.<sup>1,2</sup> The PVC particles are approximately 1  $\mu\text{m}$  and smaller. It also contains agglomerated particles which are in an order of 10  $\mu\text{m}$ .<sup>3</sup> A variety of process in fabricating plastisol into flexible products include dip coating, slush molding, rotational molding, roller or knife-edge coating, fabric coating, and foam preparation. Common features in all these processes are: first, plastisol is coated on a substrate, and then, heat-set in an oven at about 200°C. The transformation of plastisol paste to rubbery substance during heating is known as gelation and fusion.

In our previous works, viscoelastic methods were employed to follow a buildup of modulus during gelation and melting of crystallites in fusion stage.<sup>4,5</sup> Concurrently, a scanning electron microscopy (SEM) was used to observe the swelling of PVC particles and eventual disappearance of the particulate structure.<sup>4,5</sup>

The present work is the *in situ* observation of swelling of PVC particles during gelation and fusion with small-angle light scattering (SALS). Although the viscoelastic measurements were made with a very small amplitude of oscillation so as not to disturb the system, there is a possible chance that the mechanical work may influence the swelling behavior. At least one such influence of mechanical oscillation on the behavior of hydrogel was reported.<sup>6</sup> Also, the phase solubility of a polymer blend was found to be affected by the appli-

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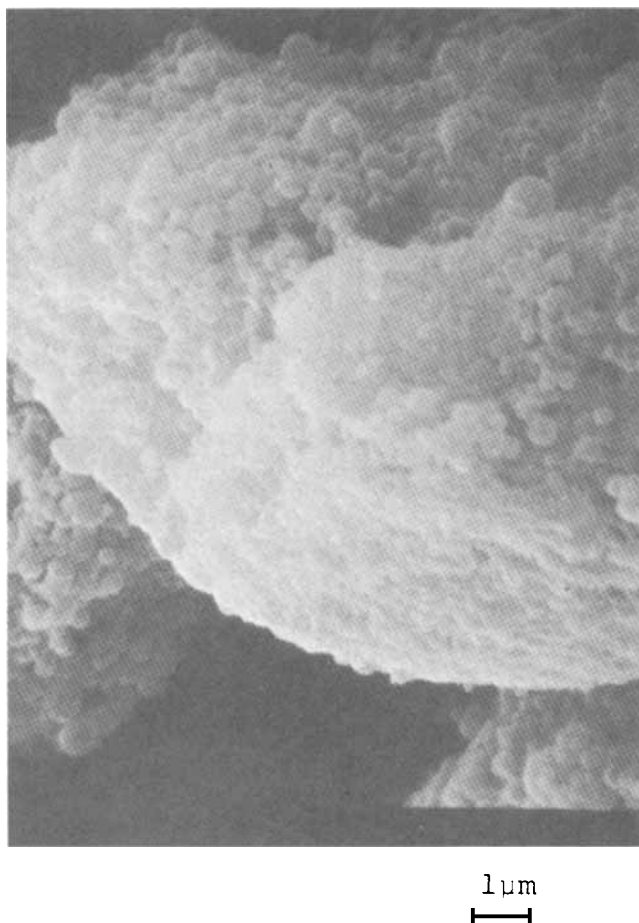


Fig. 1. Agglomerated particle of dispersion PVC exposing primary particles at broken surface;  $7500\times$  with scanning electron microscopy.<sup>3</sup>

cation of a steady shear stress.<sup>7</sup> The light scattering, being a quiescent method, it is free from mechanical perturbation.

The SEM procedure requires a rapid cooling of specimen, freeze-fracturing, and other sample-preparation; thereby it might alter the transient morphology of the sample. Because light scattering is conducted *in situ* during the gelation and fusion, possible artifacts can be avoided.

In this work one typical plastisol grade of PVC and three different plasticizers were used. Plasticizers, diethylhexylphthalate (DOP), dibutylsebacate (DBS), and dioctylsebacate (DOS), were selected to represent a range of solvent power.

## MATERIALS AND METHODS

### Particulate Structure of PVC

The plastisol grades of PVC, "dispersion resins," are made with emulsion polymerization and subsequent spray drying. In the latter process some particles

TABLE I  
Plastisol Formulation

Component	Parts by weight
Resin, Geon 121 <sup>a</sup>	100
Plasticizer	57
Epoxidized soybean oil	3
Barium, cadmium, zinc stabilizer	2

<sup>a</sup> Registered trade-mark of BF Goodrich Co.

become agglomerated. The larger agglomerates are ground to the size smaller than 20  $\mu\text{m}$ . Figure 1 depicts the scanning electron microscope (SEM) photograph of an agglomerate, and its fractured surface showing primary particles imbeded together.<sup>3</sup> The commercial dispersion resin used for this work has approximately bimodal particle size distribution. The larger particles are in a range of 8–25  $\mu\text{m}$  and the smaller ones are in the size smaller than 2  $\mu\text{m}$ .<sup>3</sup> The larger-size fraction may be about 15–18%, but the amount decreases during handling because some of the agglomerates are quite friable.<sup>3</sup>

A formulation used for this work is given in Table I. Figure 2 is an optical microscope photograph of the plastisol, where agglomerated particles may be identified.

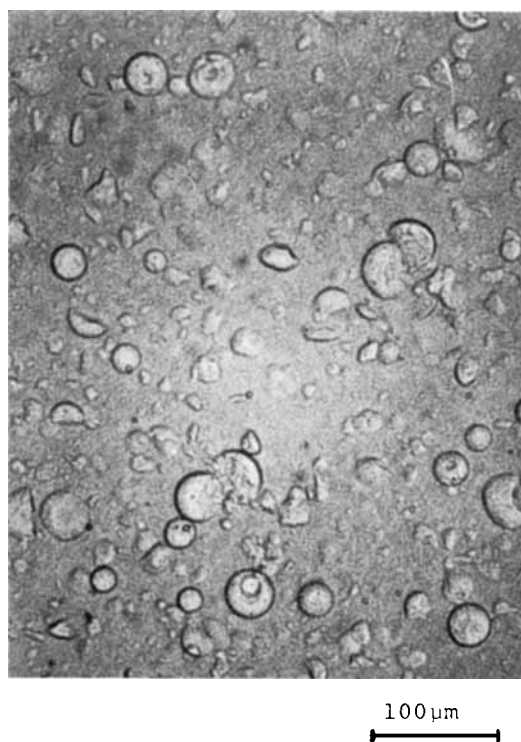


Fig. 2. PVC plastisol observed with optical microscope, showing agglomerated particles.<sup>3</sup>

At ambient temperature plastisol is white and opaque. When it is heated, it becomes translucent at temperature above  $T_g$ . This happens when the interstitial voids are completely filled with plasticizer. Above  $T_g$  the primary particles of PVC swell progressively with the increase of temperature until the particulate structure disappears to form a uniform mass. Figure 3 shows an SEM photograph of particulates which are swollen with plasticizer.<sup>8</sup> As seen in Figure 3, the primary particles are packed together. A previous work with differential scanning calorimeter (DSC) indicated that during gelation there are two different phases, a PVC-rich phase representing particles in a process of swelling and the plasticizer-rich phase containing dissolved polymer.<sup>9</sup> When there is sufficient difference in refractive indices between two phases, the SALS measurement is expected to give quantitative measure of the swollen PVC particle size.

### Instrument

A time-resolved light scattering setup, schematically shown in Figure 4 was utilized. It consists of a laser light source (He-Ne laser with a wavelength of 6328 Å), a set of polarizer and analyzer, a sample hot stage, and a screen. Scattered patterns from polymers may be photographed using a Polaroid instant camera (Polaroid Land Film Holder 545). The scattered intensity can be quantitatively monitored by means of a 2-dimensional Vidicon camera (1254 B, EG&G Co.) coupled with a detector controller (Model 1216, EG&G Co.). The analog signal is digitized and analyzed on an OMA III (Optical Multichannel Analyzer) system. The scan rate is typically 30 ms for 1-dimensional scan and

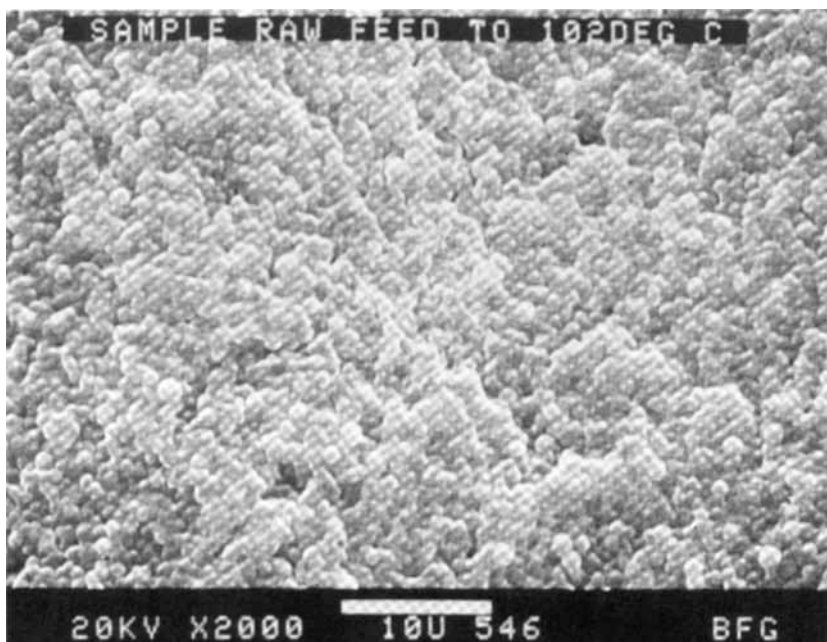


Fig. 3. PVC plastisol in the process of gelation at 120°C showing the particulate structure.<sup>8</sup> Courtesy of *Polymer Journal*.

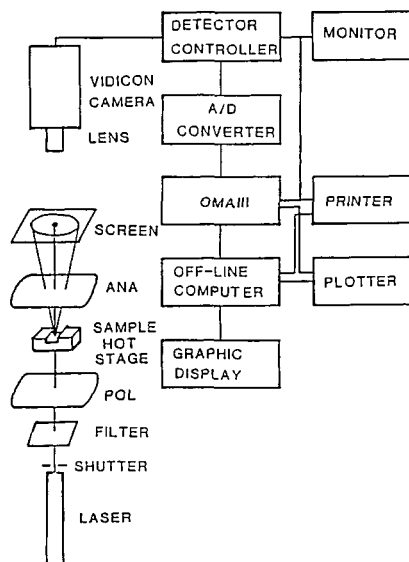


Fig. 4. A schematic of small angle light scattering setup.

about 0.5–1.5 s for 2-dimensional mode depending on the number of pixels chosen for grouping. Various modes of data acquisition are available for selection to commensurate with experimental configurations. The raw data are further transferred to an off-line computer (IBM-XT) for post-data treatments such as background correction, data smoothing, rescaling, etc. In the present study, no polarizers were used.

Intensities of scattered light were acquired as a function of incremental temperature. Background corrections were carried out and then the intensity profiles were stored in a floppy disk. Samples were heated at 5°C/min; because the swelling of plastisol is not an equilibrium phenomenon, the heating rate affects the degree of swelling. The heating rate of this work was an arbitrary choice. However, our previous work on viscoelastic properties indicated that the swelling is very slow and at a given temperature it is in quasiequilibrium.<sup>4</sup>

## RESULTS

The variations in scattering intensity are plotted as a function of scattering wavenumber  $q$  for the DOP system in Figure 5;  $q = [4\pi \sin(\theta/2)]/\lambda$ , where  $\theta$  and  $\lambda$  are the scattering angle and wavelength of light in the medium. The scattering intensity shows no maximum on the  $q$ -axis and decays with increasing value of  $q$ . As the temperature is raised from 110 to 130°C, significant increases in the scattering intensity occurred. As shown in Figure 6, the scattering intensity increases with temperature in two steps. It shows a slight increase past  $T_g$ , i.e., 80°C, increases again to a maximum, and then decreases. This is the temperature range where gelation and fusion of PVC plastisols occur. This observation is in good accord with that observed by viscoelastic methods.<sup>4</sup>

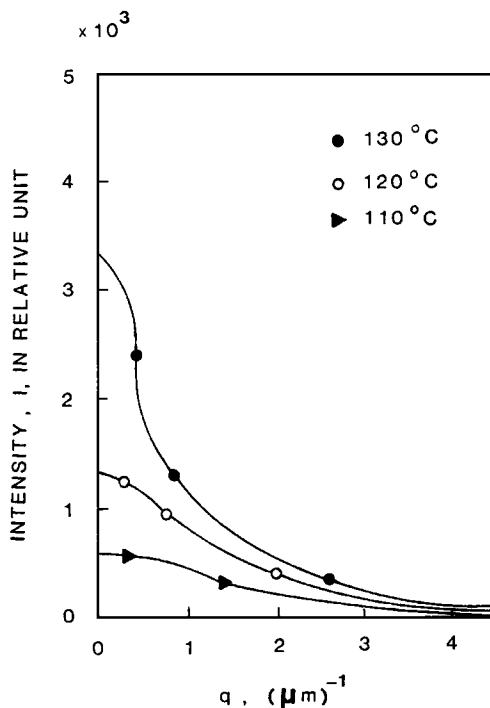


Fig. 5. The variation of scattering intensity as a function of scattering vector  $q$  at 110 ( $\blacktriangleright$ ), 120 ( $\circ$ ), and 130°C ( $\bullet$ ) for PVC-DOP system.

Debye and Bueche<sup>10</sup> gave the following relationship between the scattering intensity  $I$  and scattering wavenumber  $q$ :

$$I^{-1/2} = K_1^{-1/2}(1 + a_1^2 q^2)/a_1^{3/2} \quad (1)$$

where  $K_1$  is a constant and  $a_1$  is the short-range-correlation distance. This plot for the DOP system is shown in Figure 7, which gave straight-line relationships. The short-range-correlation distances  $a_1$  are obtained from the slope and intercept of these plots by the method of least-square fitting.

Guinier's approximation<sup>11</sup> gives another relationship between  $I$  and  $q$  as follows:

$$\ln I = \ln(K_2 \cdot a_2^3) - a_2^2 q^2/4 \quad (2)$$

where  $K_2$  is a constant and  $a_2$  is a long-range-correlation distance. For this plot a straight-line relation is expected only in a range of small values of  $q^2$ . Guinier plots of the DOP system are shown in Figure 8; the  $a_2$  values were obtained from the slope of the lines as shown in the figure.

The correlation distances,  $a_1$  and  $a_2$ , are plotted as functions of temperature for the three plasticizer systems and presented in Figures 9–11. The reliable data are obtained starting at 70–80°C, where the plastisols change from opaque to translucent. The upper cutoff temperature of the observation was 140–150°C,

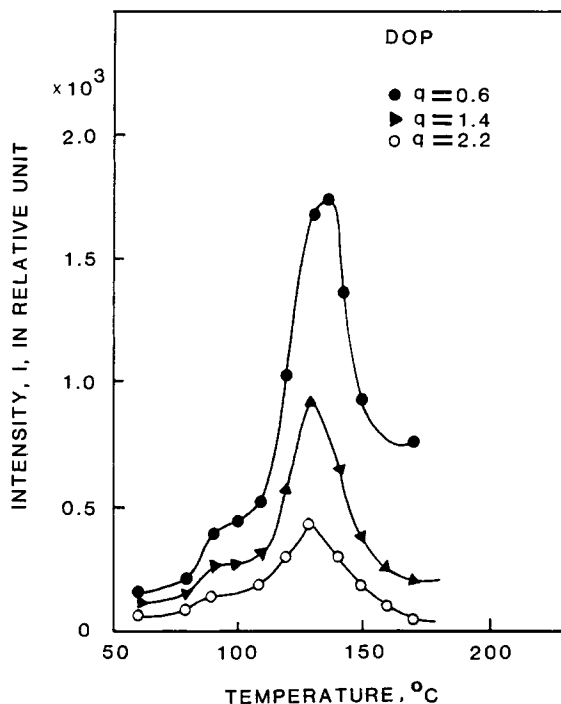


Fig. 6. The variation of scattering intensity as a function of temperature at different  $q$  for PVC-DOP system: (●) 0.6; (▴) 1.4; (○) 2.2.

where particulates begin to lose their identity and, therefore, the signal decreases.

## DISCUSSION

As shown in Figure 3, the particles of PVC are packed very closely. The correlation distances,  $a_1$  and  $a_2$ , may be regarded as measures of the particle sizes, which indicate degree of swelling. Therefore, the short-range-correlation distance  $a_1$  represents an average size of relatively smaller particles and the long-range correlation distances  $a_2$  represents an average size of relatively larger particles. Because the particle-size distribution is very broad,<sup>3</sup> both  $a_1$  and  $a_2$  are average values.

The glass transition temperature of the sample PVC of this work is 80°C. When the plastisol made with this resin and DOP, several significant behavior changes occurred around this temperature.<sup>4</sup> When the plastisol film is heated on the temperature-gradient plate, it assumes a dry appearance at about 80°C. Also, the system changes from a viscous paste to a coherent mass which may be peeled off from the plate, although its strength is very low.<sup>5</sup> Further, DSC measurements revealed the following; when the above plastisol is heated to slightly below 80°C in the first scan, the glass transition of PVC remains intact in the second scan. This means that the resin particles at 80°C are not swollen with DOP, although some swelling at the surface of the particles may have

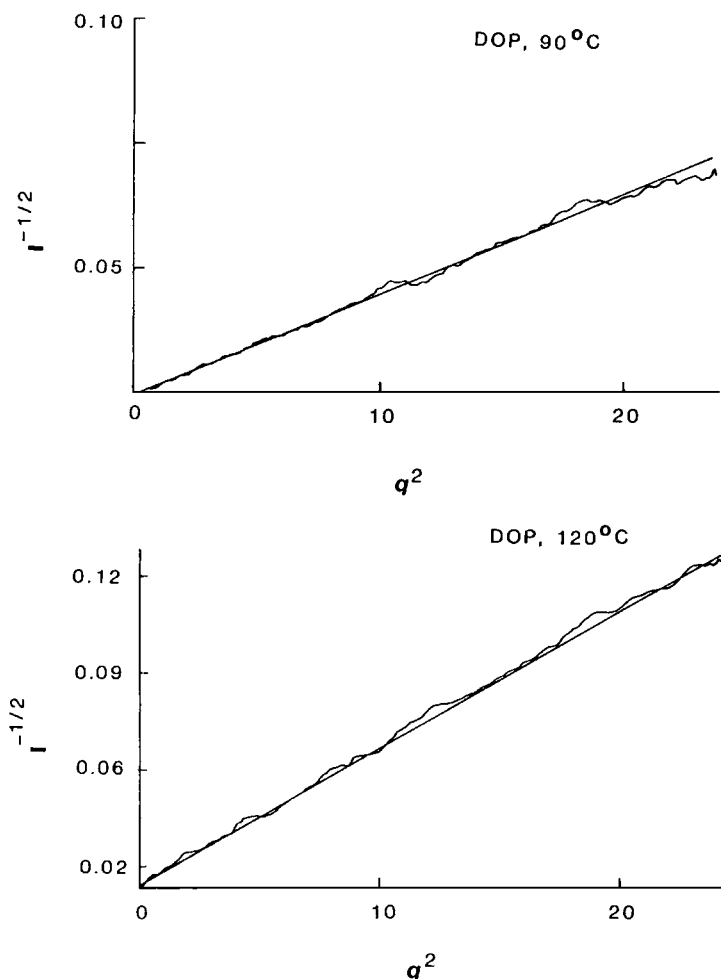


Fig. 7. Debye-Bueche plot for PVC-DOP system at 90 and 120°C.

occurred. However, if it is heated to 85°C in the first scan, the glass transition of PVC disappears completely in the second scan.<sup>9</sup> Apparently, the interior of PVC particle is affected by DOP diffusing into it. Since at 80°C the storage modulus is high but the interior of PVC particles is not affected by DOP, the plasticizer must be filling the interstitial voids.<sup>4,5</sup> With this background information, the SALS results of Figures 9–11 will be interpreted. With PVC-DOP system at 80°C values of  $a_1$  and  $a_2$  are 0.28 and 0.74  $\mu\text{m}$ , respectively (Fig. 9). The  $a_2$  value is in good agreement with the median particle size of the unswollen resin, 0.58–0.78  $\mu\text{m}$ , which had been characterized with a sedimentation method.<sup>3</sup> However, this method was not extended to cover the size smaller than 0.37  $\mu\text{m}$ . The amount of particles smaller than 0.37  $\mu\text{m}$  (ultrafine) was about 12.5% of the resin.<sup>3</sup> This is a significant fraction. Although in principle the sedimentation method may be used to cover this size range, it takes an excessive time to be realistic. The value of  $a_1$ , 0.28  $\mu\text{m}$ , indicates the presence of the particles smaller than what was observed by sedimentation. Because the ul-



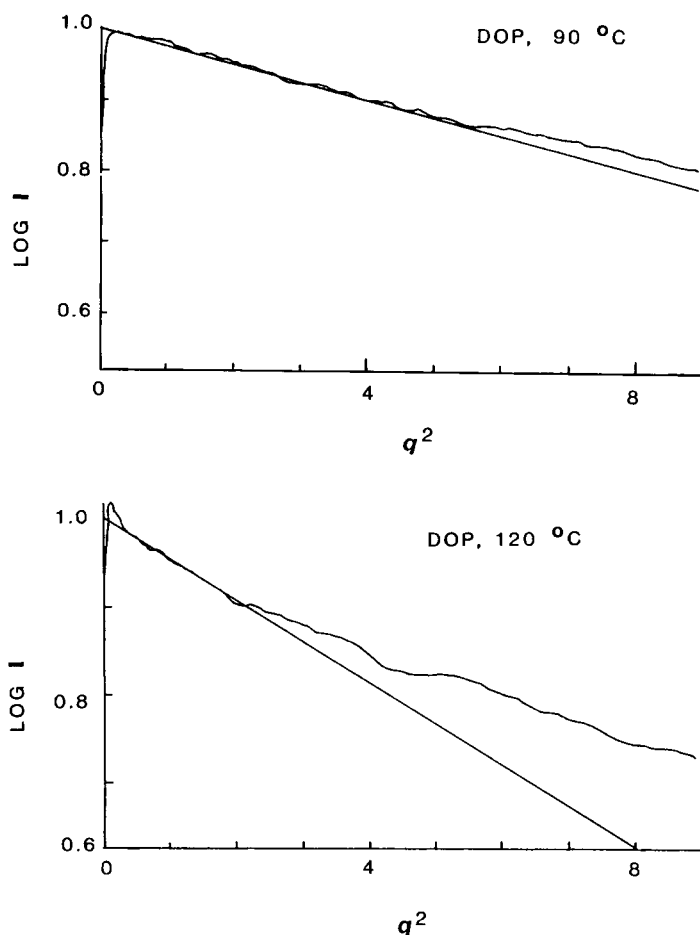


Fig. 8. Guinier plot for PVC-DOP system at 90 and 120°C.

trafine particles are known to affect rheology of plastisol at room temperature,<sup>3</sup> uses of SALS offers a useful method of characterization of ultrafine particles.

Also the sizes of swollen particles as evaluated by SALS are in agreement with those observed with SEM.<sup>4,5</sup> However, in the latter method a quantitative measurements of the swollen size are rather difficult and not very accurate. Therefore, SALS offers a unique advantage in this regard. With PVC-DOS system the values of  $a_1$  and  $a_2$  at 80°C are very similar to those of PVC-DOP system. However, with DOS the swelling is minimal up to 130°C and then increases significantly. The largest value of  $a_2$  is for DOP system 1.45  $\mu\text{m}$  at 140°C and for DOS 1.25  $\mu\text{m}$  at 150°C. Overall, DOS is a poorer solvent as compared to DOP. This was also indicated in the previous study of viscoelastic properties over the corresponding temperature range.<sup>4</sup> The plasticizer, DBS, is known to be a better solvent for PVC; for example, in the first scan with DSC this plasticizer lowered  $T_g$  of PVC by several degrees. With no other plasticizer of this study,  $T_g$  of PVC was affected in the first scan. At 70°C the values of  $a_1$  and  $a_2$  are 0.38 and 0.87, respectively. These values are already somewhat higher than those expected for the unswollen particles. Between 70 and 80°C

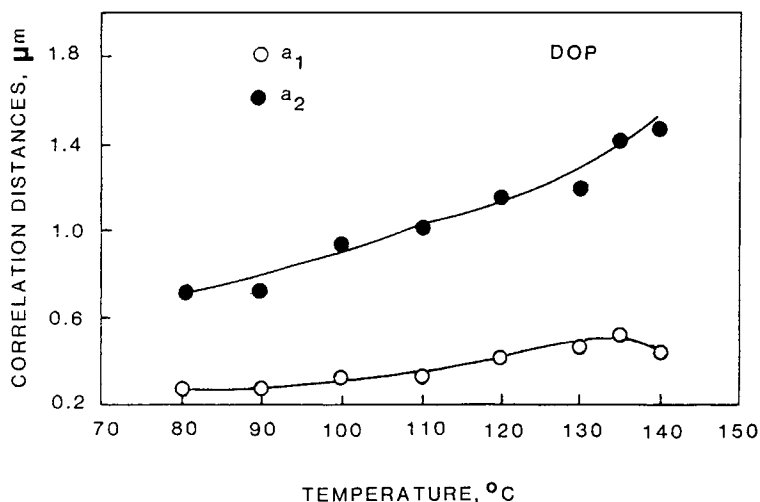


Fig. 9. Change of short-range-correlation distance  $a_1$  ( $\circ$ ) and long-range-correlation distance  $a_2$  ( $\bullet$ ) with temperature; PVC-DOP system.

there are significant increases, indicating that swelling has taken place. Over the entire temperature range of observation the values of  $a_1$  and  $a_2$  are significantly larger than those for DOP system.

## CONCLUSIONS

The SALS method is shown to provide a quantitative measure of changes in PVC particle size during gelation of PVC plastisol. Although SEM also show the particles in the process of swelling, the quantitative evaluation of the particle

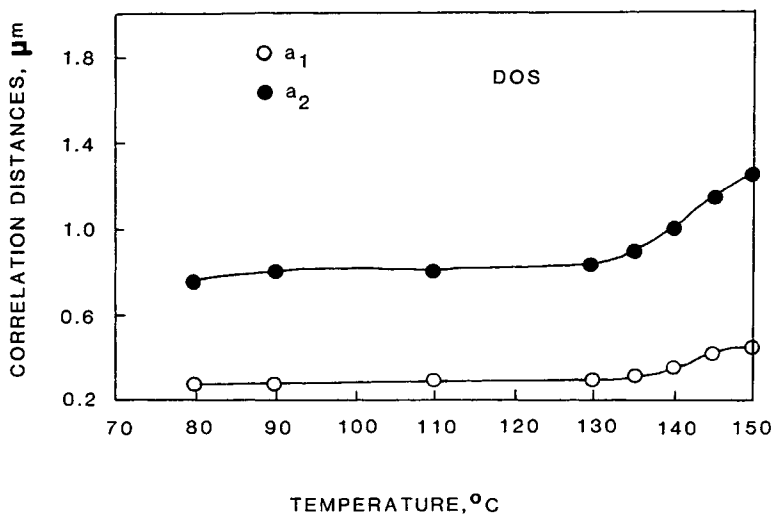


Fig. 10. Change of  $a_1$  ( $\circ$ ) and  $a_2$  ( $\bullet$ ) with temperature; PVC-DOS system.

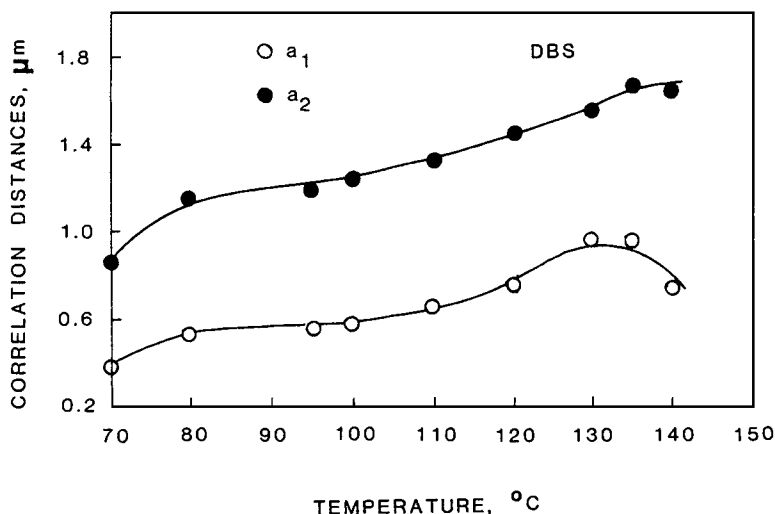


Fig. 11. Change of  $a_1$  (○) and  $a_2$  (●) with temperature; PVC-DBS system.

size is rather difficult and inaccurate. The SALS also provides means of characterizing the unswollen particle size; a particular advantage is the characterization of size of ultrafine particles for which sedimentation method takes too long and, therefore, impractical. With the use of SALS and from the results of extent of swelling at a given temperature the relative solvent power of plasticizer may be evaluated.

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