

Structural Characteristic of Poly (vinylacetate) Microgel in Solution

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The polyvinylacetate microgel was prepared by emulsion-copolymerization with various contents of butan-1,4-divinylether (BVE). The introduction of BVE was found to reduce the sol fraction, and the resulted microgel revealed more compact structure with increasing the BVE content from its dilute solution properties. The chain structure was qualitatively analyzed in terms of the soft-sphere model developed earlier. The synchrotron small-angle X-ray scattering revealed a spherical distance distribution of homogeneous density up to 200 Å, though cores of smaller radius (40 Å) might be distributed in the microgel sphere.

KEY WORDS: Polyvinylacetate microgel/ Emulsion polymerization /Soft-sphere model/ Dilute solution property/ Synchrotron small-angle X-ray scattering/

I. INTRODUCTION

The microgel denotes the highly branched polymer molecule of the shape and size of the latex particle, and constitutes an interesting field of materials as demonstrated by the synthetic rubber copolymerized from styrene and butadiene in emulsion.¹⁾ The microgel can be dissolved in solvent to make a homogeneous solution, while dispersed in non-solvent (water) as a hard sphere of rather homogeneous radius. The microgel may be aged or vulcanized to produce the macrogel as the form of primary reaction gel. So far investigated was the microgel produced by the polymerization of divinyl- or diene-compounds. Much interest was paid to the microgel emulsion-polymerized from divinylbenzene where the unreacted double bond may be utilized in the succeeding steps of reaction.²⁾

The gelation is also possible through the chain transfer reaction in the emulsion-polymerization of monovinyl-compounds. For example, emulsion polymerization of vinylacetate results at higher monomer conversion (over 80 %) the formation of gels because of the high chain transfer constant of the acetate groups.³⁾ The systematic characterization was performed with poly(vinylacetate) (PVAc) microgels prepared by the polymerization of

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vinylacetate in emulsion with high monomer conversions.⁴⁾ Here the gelation in the microphase leads to the formation of latex particles of the size depending on the concentration of the emulsifying agent, the reaction temperature and the hydrodynamic conditions (stirring speed, stirring interval, etc.). For example, the radius r of a microgel latex depends on the concentration S of the emulsifying agent as

$$1/r^3 \sim S^{0.49} \quad (1)$$

However, no sol-free PVAc microgels were prepared without crosslinking agent. The sol fraction deteriorates the characteristics of microgels as primary reaction gel to produce macrogels applied in industrial fields, and the separation of the sol fraction from microgels is troublesome. According to Heitz's scheme⁵⁾ PVAc microgels were prepared through the copolymerization of vinylacetate (VAc) with butane-1,4-diol-divinylether (BVE) to reduce the sol fraction in resulted microgels. This copolymerization produces microgels of various branching densities according to the BVE content. We examine in this report the dilute solution properties of the microgels as a function of the BVE content.

II. Experimental Part

2.1. Microgelation by Copolymerization of VAc and BVE

Eight PVAc microgel samples were prepared by the emulsion copolymerization of vinylacetate (VAc) and butane-1,4-dioldivinyloether (BVE) at 40°C where the BVE content was varied from 0.001 to 1.0 vol. %. When the BVE content exceeds 1 vol. %, then the resulted PVAc microgel does not dissolve in solvent. Water phase and oil phase of vinylacetate were mixed in the volume ratio 7:1 where water phase contains 0.32 % emulsifying agent consisting of Na-cetyl sulfate, cetyl alcohol and dioctyl-Na-sulfosuccinate in mole ratio 4:1:1, 0.2 % NaHCO₃ and 0.14 % Na₂S₂T₂ + (NH₄)₂S₂O₈ as an initiator. VAc monomer almost free from acetaldehyde, supplied by the courtesy of Dr. Schmidhammer (Wacker Co., W. Germany), was prepared by the gasphase-acetoxylation of ethylene. VAc was fractionally distilled under nitrogen 5.5 (Messer-Griesheim, purity >99.9995 vol. % and O₂ ≤ 0.5 vpm) through the 40 cm-high mirror-coated column with a vacuum jacket connected to the 20 cm-high column filled with Raschig rings for better fractionation efficiency. The main fraction was repeatedly distilled till no trace of acetaldehyde was observed by UV-spectroscopy. Freshly distilled VAc was kept at -16°C at most 2 weeks under nitrogen in a dark room till used for polymerization. The boiling point of VAc was between 72.3 and 72.9°C at atomospheric pressure.

Commercial butane-1,4-dioldivinyloether (BVE) (Merck-Schuchardt, W. Germany) was washed 3 times with 1N NaOH solution to remove the stabilizer and dried over sodium sulfate. BVE was then dried again over KOH. Predried BVE monomer was left over metal sodium wire for 24 hours in prior to its distillation through a Vigreux-column under the reduced pressure of nitrogen 5.5 atomosphere by a water suction pump. A UV-spectrum showed no trace of aromatic impurities. The boiling point of BVE was 38°C at 5 mmHg.

Water was bidistilled under nitrogen 5.5. atomosphere Commercial Na-cetylsulfate (Merck, W. Germany) and cetylalcohol (Roth, W. Germany) were used for polymerization without further processing. Dioctyl-Na-sulfosuccinate (Merck), sodium disulfide (Roth) and

ammonium peroxodisulfate (Merck) were also used directly.

Each emulsion polymerization was taken place under nitrogen 5.5 atmosphere in a Juvo Ju D25/2 1l vessel coupled with a pressure-stirrer D25/2. A reaction temperature was regulated to 40°C by circulating methanol of constant temperature. The details of the polymerization procedure should be consulted with the ref.⁴⁾

Resulted PVAc microgels were transferred into sufficient amount of ice water containing hydrochloric acid (2-5ml conc. HCl in 100ml water), and neutralized with alkali after a short period. The solutions were left overnight at 4°C and the coagulated spongecake-like PVAc microgels were then separated by filtration. PVAc microgels in the filter were washed with ice water till no bubble was observed. Washed and pressed microgel samples were dissolved in methanol and precipitated in ice water. Precipitated microgels were washed in the filter with ice water and pressed for further processing. These processes were repeated 3 times. Finally pressed microgel samples were dried in a desiccator by evacuating to $10^{-2} \sim 10^{-3}$ Torr. The samples were stored at -16°C in a dark room till used in order to prevent further crosslinking.

2.2. Characterization of PVAc Microgel

2.2.1. Intrinsic viscosity

Intrinsic viscosities of PVAc microgels were estimated from the viscosities of five methanol solutions of PVAc microgels in the concentration range between 1g/l and 20 g/l, measured at 20°C with an Ostwald-type viscometer. Each solution was cleaned through a G3- or G4-glassfilter in prior measurements.

2.2.2. Partial specific volume

The PVAc microgel-methanol solutions of five different concentrations ($c=2.5\text{g/l} \sim 20\text{g/l}$) were cleaned through a G3- or G4-glassfilter. The specific densities of these solutions and solvent were measured at 20°C with a Vibrationsdensitometer (A. Paar K.G., Graz) and the average specific volumes were calculated from the following equation:

$$\bar{v} = (1/d_{MeOH}) \left(1 - \frac{d_{PVAcSol.} - d_{MeOH}}{c} \right) \quad (2)$$

2.2.3. Light scattering

The light scattering measurements were performed with a Sofica-Photogoniometer Model 42000, equipped with an Oriel-optic which enables the scattering measurements with a UV-light ($\lambda_0=365$ nm). Optically clean solutions of PVAc microgels in methanol were prepared by centrifugation (20,000 rpm) or filtration through a G4-or G3-glassfilter. The scattered intensities of each solution were recorded for 29 angles from 20°C to 150° (every 2.5° for 20°~30° and every 5° for 30°~150° at 20°C respectively with a blue-light ($\lambda_0=436$ nm) and a UV-light ($\lambda_0=365$ nm). The refractive index increment of the PVAc-methanol solution was determined as

$$dn/dc = 0.1419 \text{ (for } \lambda_0 = 436 \text{ nm)} \quad (3)$$

with a Brice-Phoenix Differentialrefractometer. The data were analysed according to Zim:⁶⁾

$$Kc/I(q) \sim 1/(P_z(q)\bar{M}_w) + 2A_2c + \dots \quad (4)$$

and the radius of gyration of PVAc microgels were estimated from the initial slope of the Zimm-plots:

$$P_z(q)^{-1} \sim 1 + q^2 \langle S^2 \rangle_z / 3 \quad (5)$$

The Guinier approximation⁷⁾

$$P_z(q) \sim \exp(-q^2 \langle S^2 \rangle_z / 3) \quad (6)$$

was used to estimate the latex size of PVAc microgels in emulsion. Here K , $I(q)$, $P_z(q)$, $\bar{M}_w$ and A_2 denote the optical constant, the reduced scattered intensity from solute, the z average particle scattering factor, the *weight* average molecular weight, the second virial coefficient and the z average mean-square radius of gyration, respectively. The magnitude of the scattering vector q is defined in terms of the scattering angle θ and the wave length λ of the incident beam as

$$q = (4\pi/\lambda) \sin \theta \quad (7)$$

2.2.4. Small-angle X-ray scattering

The small-angle X-ray scattering (SAXS) measurements from PVAc microgel-methanol solutions were performed with a focusing optics SAXES (Small-Angle X-ray Equipment for Solutions) installed at the 2.5 GeV storage ring in Photon Factory of National Laboratory for High Energy Physics at Tsukuba.⁸⁾ The scattered intensity $I(q)$ was then Fourier-transformed to yield the distance distribution function:

$$p(r) = \frac{1}{2\pi^2} \int_0^\infty I(q) \cdot (qr) \cdot \sin(qr) dq \quad (8a)$$

which is related to the characteristic function $g(r)$ as

$$p(r) = 4\pi r^2 g(r) \quad (8b)$$

Here the scattered intensity was extrapolated to both the zero angle and the larger scattering vectors according to the Guinier's approximation (eq. (6)) and Porod's forth-power law:⁹⁾

$$I(q) \propto I(0)/q^4 \quad (9)$$

respectively in order to eliminate the termination effect in the Fourier transformation. Eq. (9) implies that the background scattering is constant with respect to the scattering angle in the measured angular range. The radius of gyration of the rod cross-section $\langle S_{cs}^2 \rangle^{1/2}$ was estimated from the innermost part of the scattered intensity according to the equation:⁹⁾

$$qI(q) \propto \exp(-q^2 \langle S_{cs}^2 \rangle / 2) \quad (10)$$

2.2.5. Gel Permeation Chromatography

A 50 cm-high column was used for the gel permeation chromatography (GPC) where the inner diameter of the column was 2 cm. Various combinations of silica gels of the specified pore size between 1000 Å and 25000 Å (Fractosil, Merck) were employed according to the fractionation condition. Distilled methanol over CaH₂ was served as a carrier.

III. Results and Discussion

The molecular weights and latex particle weights of PVAc microgels were estimated by light scattering as summarized in Table 1. Here the latex particle weights were calculated

Table 1. Molecular Weight and Latex Particle Weight of KVAc Microgel

PVAc-No.	BVE content ^{a)} (vol. -%)	$M_L \times 10^{-6}$ ^{b)} (g/mol)	$\bar{M}_w \times 10^{-6}$ ^{c)} (g/mol)	m_g ^{d)} ($\equiv \bar{M}_w/M_L$)
182	1	368	330	89.7
223	1	196	167	88.1
200	0.5	742	603	81.3
222	0.5	207	125	60.5
183	0.1	380	300	78.9
184	0.05	350	258	73.8
221	0.01	412	183	44.4
185	0.001	188	38.3	20.4

a) vol. -% at 40°C

b) calculated by $M_L = (4\pi r^3/3)N_L/\bar{v}$ with $r = (5\langle S^2 \rangle_z/3)^{1/2}$
(see eqs. (11) and (12).)

c) measured at 20°C in methanol by light scattering

d) the microgel fraction defined by $m_g \equiv \bar{M}_w/M_L$

through the equation :

$$M_L = (4\pi r^3/3)N_L/\bar{v} \quad (11)$$

$$r = (5\langle S^2 \rangle_z/3)^{1/2} \quad (12)$$

using $\langle S^2 \rangle_z$ estimated from the Wesslau-plots¹⁰⁾ (see eq. (6)) of the light scattering data of PVAc/BVE microgel emulsions where a hard sphere of a radius r was assumed for a PVAc/BVE latex and N_L denotes Loschmidt's number ($N_L = 2.6869 \times 10^{19}$). The Wesslau-plots yielded a good linearity confirming the compact sphere shape of PVAc/BVE latexes. The molecular weight of a microgel should be equal to the latex particle weight estimated here if the microgel is perfect and contain no sol fraction. Thus the ratio of the molecular weight to the latex particle weight indicates the gel fraction m_g in a latex, and consequently the sol fraction by $1 - m_g$. Table 1 shows that the PVAc/BVE microgel contains less sol fraction with increasing a BVE content as expected. This trend is traced more quantitatively by the GPC-elution curves (Fig. 1). The gel fraction (m_g) and sol fraction (m_s) estimated from GPC are summarized in Table 2. The agreement between two independently estimated values of m_g is satisfactory when considered a large error involved in separating sol- and gel- portions in the GPC curves. The density of the PVAc/BVE microgel is also expected to increase and to be less swollen in solvent as the BVE content increases. Fig. 2 exhibits the specific volume of the PVAc/BVE microgel in methanol as a function of the BVE content. The specific volume in methanol decreases 5 % by introducing 1 vol. % BVE in the microgel. The swelling degree can be expressed in terms of a radial expansion q or a volume expansion q^3 defined as

$$q = \langle S^2 \rangle_{z,P} / \langle S^2 \rangle_{z,L} \quad (13)$$

where $\langle S^2 \rangle_{z,L}$ and $\langle S^2 \rangle_{z,P}$ denote the z average radius of gyration of the latex particle

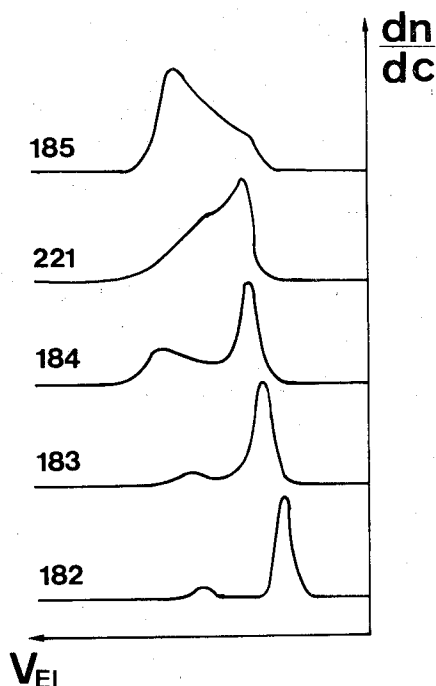


Fig. 1. GPC-elution curves of PVA3/BVE microgels. The sample numbers are shown in the figure.

Table 2. Sol and Gel Fraction of PVAc Microgel

PVAc-No.	BVE content ^{a)} (vol. —%)	$m_g^{b)}$ (%)	$m_s^{c)}$ (%)
182	1	88.9	11.1
183	0.1	85.7	14.3
184	0.05	53.2	46.8
221	0.01	39.6	60.4
185	0.001	10.9	89.1

a) vol. —% at 40°C

b) Microgel fraction estimated from GPC. c) Sol fraction = $1 - m_g$

in emulsion and that of the PVAc/BVE microgel dissolved in methanol. The swelling degree depends on the BVE content, i.e., the branching density, as summarized in Table 3.

The PVAc/BVE microgel is seen to maintain its spherical shape in methanol (Fig. 3). The scattering curves of these microgels in methanol are qualitatively explained in terms of a soft-sphere model composed of approximately 3~8 shells.¹¹⁾ The second virial coefficients A_2 of the PVAc/BVE microgels in methanol at 20°C is in proportion to $1/\bar{M}_w$ as expected from the theory of the second virial coefficient of rigid spheres (see Fig. 4):

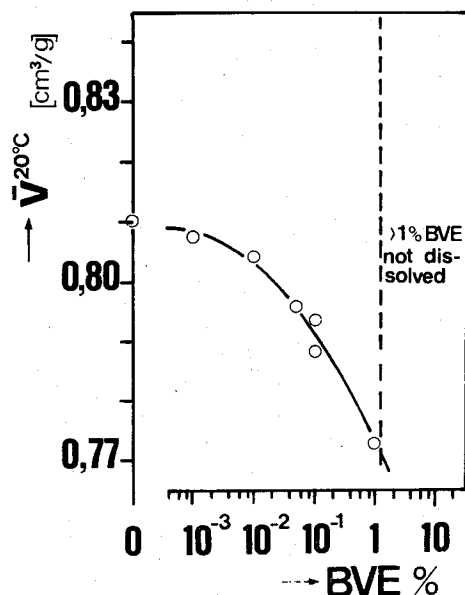


Fig. 2. Specific volume of the PVAc/BVE microgel in methanol at 20°C as a function of the BVE content.

Table 3. Swelling Degree of PVAc Microgel

PVAc-No.	BVE content ^{a)} (vol. —%)	$\langle S^2 \rangle_{z,L}$ $\times 10^{10}$ ^{b)} (cm ²)	$\langle S^2 \rangle_{z,p}$ $\times 10^{10}$ ^{c)} (cm ²)	$q^{3,d)$	$q^e)$
182	1	0.140	0.363	4.18	1.61
223	1	0.090	0.212	3.62	1.54
200	0.5	0.225	0.692	5.41	1.76
222	0.5	0.096	0.290	5.25	1.74
183	0.1	0.145	0.578	7.96	2.00
184	0.05	0.138	1.048	20.9	2.76
221	0.01	0.155	1.342	25.5	2.94
185	0.001	0.092	1.417	60.5	3.93

a) vol. —% at 40°C

b) the z-average radius of gyration of the latex particle in emulsion

c) the z-average radius of gyration of PVAc microgel dissolved in methanol

d) the volume expansion

e) the radial expansion

$$A_{2,sphere} = 4RT\bar{v}_{sphere}/M_{sphere} \quad (14)$$

The second virial coefficients of the PVAc homopolymer-microgels also depends linearly on $1/\bar{M}_w$ when $\bar{M}_w$ exceeds 10^7 , indicating the spherical shape of the PVAc microgel. The core part of the spherical microgel seems hard from the view point of thermodynamic interaction.

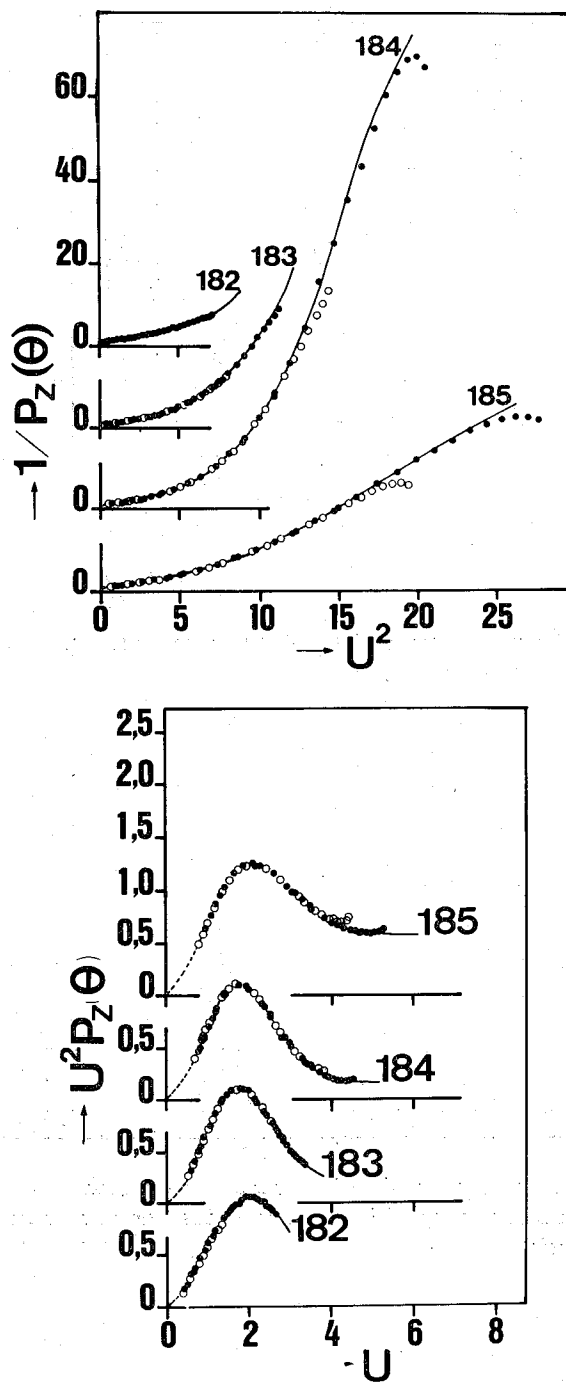


Fig. 3. (a) Zim-plots and (b) Kratky-plots of light intensities scattered from PVAc/BVE microgels in methanol. Sample Nos. are indicated in the figure.

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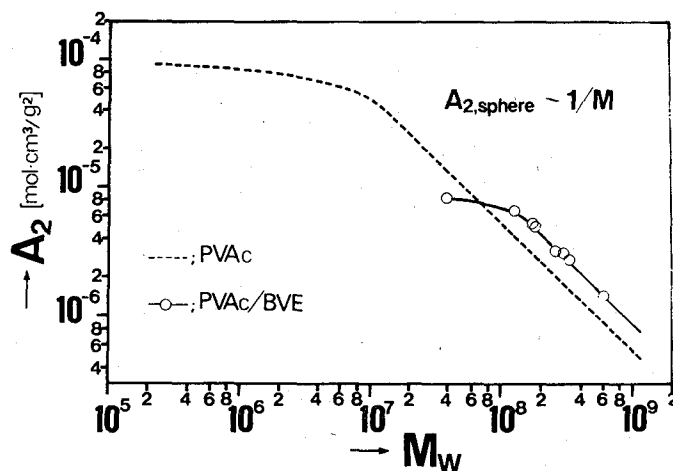


Fig. 4. Second virial coefficients of PVAc microgels as a function of the weight-average molecular weights.

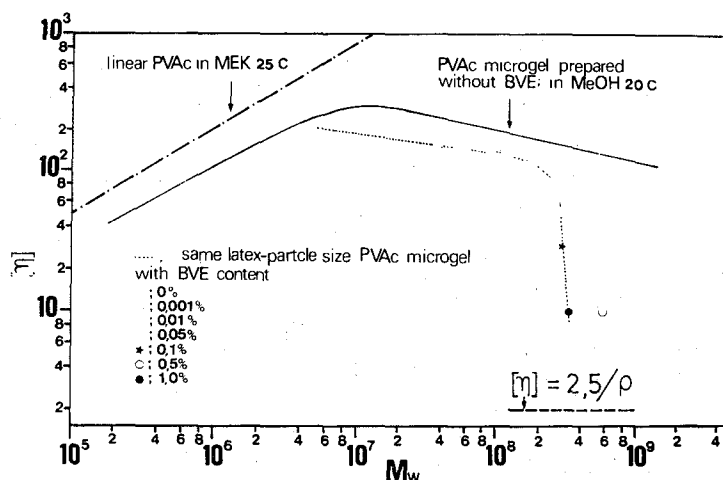


Fig. 5. Molecular weight dependence of the intrinsic viscosity $[\eta]$ of PVAc/BVE microgel

The intrinsic viscosity $[\eta]$ of the PVAc/BVE deviates from the characteristic molecular weight dependence of $[\eta]$ of the PVAc microgel without BVE and approaches to the predicted value for a rigid sphere, when the BVE content exceeds 0.05% (Fig.5). Since the microgel precipitates for the BVE content over 1%, the rigid microgel sphere cannot be prepared with present prescription. The result suggests a suppression of the internal motion with crosslinker while the soft-sphere model theory¹¹⁾ predicts more flexibility for 3~8 shells due to its Gaussian nature.

The local chain structure is better observed by the small-angle X-ray scattering. The

distance distribution function $p(r)$ and the characteristic function $g(r)$ were computed as described in 2.2.4 after smoothing the original data with the B spline function¹²⁾. The results suggest a spherical distribution of rather homogeneous density for the PVAc/BVE microgel as demonstrated in Fig. 6. The initial envelop in $g(r)$ indicates the cores of higher density of 40Å in diameter contained in the microgel sphere, though it might be an artifact due to the cut-off effect in the large q region. The extrapolation of the $g(r)$ curve to zero yields

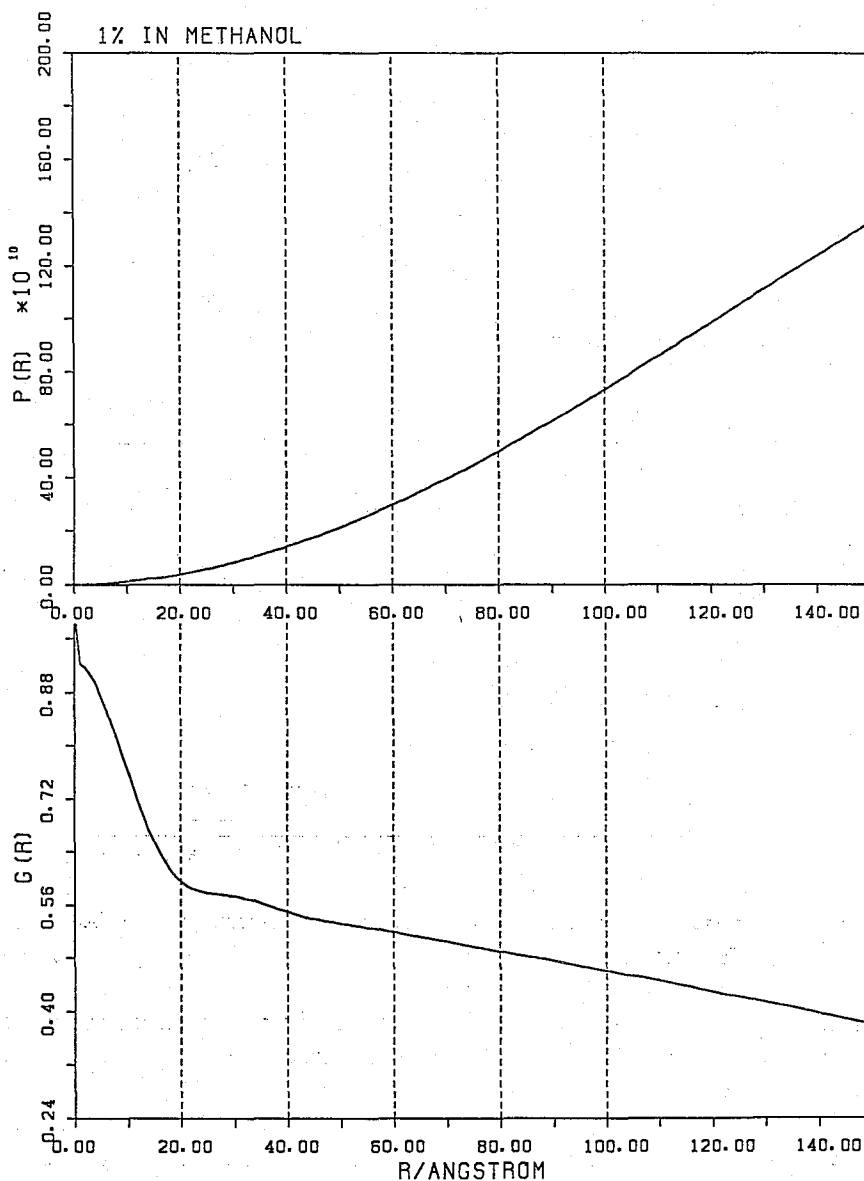


Fig. 6. Distance distribution function $p(r)$ and characteristic function $g(r)$ of PVAc/BVE microgel in methanol (PVAc No. 183)

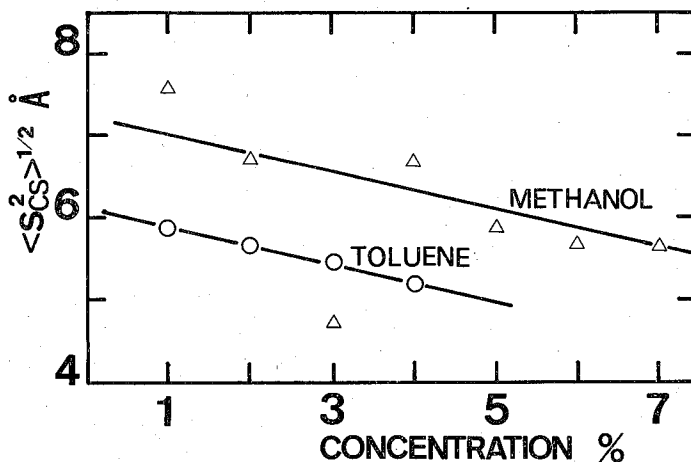


Fig. 7. Concentration dependence of the radius of gyration of cross-section of PVAc/BVE microgel in methanol and toluene (PVAc No. 183)

323 Å as the radius of the sphere which corresponds to the radius of gyration of 250 Å, much smaller than the observed value (~ 600 Å). This discrepancy is considered to be caused by the density inhomogeneity of the microgel in the order of over 100 Å as suggested by the slightly concaved shape of $g(r)$. The microgel sphere may have higher segment density towards its center. The quantitative analysis of the microgel structure requires the scattering data of much wider q ranges, including visible light and small-angle X-ray scattering measurements.

The Guinier plot for cross-section eq. (10) yielded 6~7 Å for the cross-sectional radius of gyration¹³⁾ which decreases linearly with the microgel concentration (see Fig. 7). The good linearity of the Guinier plot for cross-section suggests a local rod-like structure of microgel segments. A similar concentration dependence of the cross-sectional radius of gyration was also found in toluene solutions. The origin of this concentration dependence is unknown.

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