# Synthesis and Characterization of Thermo-Sensitive Polymeric Beads

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## Synopsis

Thermo-sensitive polymeric beads were synthesized by inverse suspension polymerization of aqueous monomer solution containing N-acryloylpyrrolidine (APR) and N,N'-methylenebisacrylamide (MBA : crosslinking agent). The polymerization conditions such as dispersion medium, dispersing agent, monomer, and initiator concentration were investigated. Fine spherical gels with diameter of 50–500 μm were obtained in high yield. The swelling volume of these gels in water continually decreased by raising atmospheric temperature and vice versa. The degree of swelling increased for the gels synthesized with lower degree of crosslinking or with lower monomer concentration at polymerization. The degree of swelling was high in water and alcohols, but the gels swelled even in nonpolar organic solvents, although the degree of swelling was low. The pore radius distribution of the gels was determined by aqueous size exclusion chromatographic method to investigate relations between pore characteristics of the gels and polymerization conditions. Monomer concentration had large effect on pore size, porosity, and pore volume of the gels. On the other hand, degree of crosslinking had little effect on these pore characteristics.

## INTRODUCTION

Several polymers with high water absorbing capacity have been developed. They are well known as hydrogels due to their gel forming property in aqueous medium. In these hydrogels, neutral amphiphilic ones are particularly interesting because they can swell both in water and organic solvents.

We synthesized N-acryloylpyrrolidine (APR), which is a derivative of acrylamide obtained by a replacement reaction of acrylamide with alkyl halide.[1] It is an amphiphilic monomer having hydrophilic amide group and hydrophobic alkylene group. The APR dissolves both in water and benzene. Poly-APR is also amphiphilic, and it has thermo-sensitive property due to its amphiphilic property. Aqueous solution of poly-APR becomes cloudy above 51°C. This temperature does not depend on polymer concentration and polymer precipitates above this temperature. Amide group in poly-APR becomes dehydration at higher temperature and polymer molecules associate with each other.[2,3]

The cross-linked poly-APR gel is expected to have a good mechanical stability and a reversible-thermal responsibility such as swelling at lower temperature and shrinkage at higher temperature.

In this article we report about the results of studies on an inverse suspension polymerization method to prepare spherical gels of cross-linked poly-APR, the

thermo-sensitive property of the gels, and a pore structure of the gels in the swelling state.

## EXPERIMENTAL

### Inverse Suspension Polymerization

APR was distilled at 83°C under a pressure of 0.2 mmHg. N,N'-methylene-bisacrylamide (MBA) as crosslinking agent, and ammonium peroxydisulfate (APS) and N,N,N',N'-tetramethylethylenediamine (TMEDA) as redox initiator system, which were guaranteed reagent grade commercial materials were used without further purification. Other chemicals were extra pure grade and used without further purification.

Dispersion solvent and dispersing agent were placed in a three-necked flask equipped with a mechanical stirrer and a thermometer. Nitrogen was slowly bubbled into the solvent for 30 min. Meanwhile, an aqueous monomer solution was bubbled with nitrogen for 15 min and APS was dissolved in the aqueous monomer solution. Then the aqueous monomer solution was poured into the dispersion medium and stirred to obtain desired droplet size. After the droplet was stabilized, TMEDA was injected into the reaction mixture and the polymerization was started. The polymerization was continued at 20°C for 2 h and the polymerization product was filtered. The polymerization product was washed first with acetone and next with methanol and then finally dried under vacuum at 40°C. The spherical polymer particles were obtained by sieving.

### Swelling Measurements

The degree of swelling and swelling volume of the polymer particles were determined by the following method and equation. Approximately 0.5 g of polymer particles was weighed, $W_1$ (g), and their volume, $V_1$ (mL), was measured. The polymer particles were swollen in the desired solvent and the volume, $V_2$ (mL), was measured at appropriate temperature.

$$\text{Degree of swelling} = V_2/V_1 \ (\text{wet-mL/dry-mL})$$

$$\text{Swelling volume} = V_2/W_1 \ (\text{wet-mL/dry-g})$$

### Exclusion Chromatographic Method

Morphological properties of the gel with particle size from 149 to 177 $\mu$m were determined by the aqueous size exclusion chromatographic method. The following components were set up for the measurements; a pump with a constant flow rate (Waters Model 510 HPLC Pump), a sample injector, a glass column (0.50 × 30 cm) equipped with a thermostatic jacket and a differential refractometer (Showa Denko Shodex RI SE-51).

The polymer particles were dipped in deionized water, degassed, and allowed to stand to swell completely for 24 h at room temperature. A column temperature was kept at 50°C. The temperature of a slurry of the gels in the deionized water was raised to 50°C and packed into the column at a flow rate of 1.0 mL/min.

Deionized water as eluent was filtered through membrane filter (0.45 $\mu$m) and degassed with ultrasonic cleaner prior to use.

The following samples were chosen to determine the calibration curve of the packed gel; dextrans and polyethylene glycols with different weight-average molecular weight, triethylene glycol, diethylene glycol, ethylene glycol and heavy water (Table I[4]). About 20 $\mu$l of aqueous solution of each sample was separately injected in the packed column at a flow rate of 0.5 mL/min and the calibration curve was determined. Finally the gel was taken out of the column, dried, and weighed, W (g).

The hold-up volume of a column, $Vd$, was measured as the elution volume of heavy water ($D_2O$) which is the smallest inert sample. The total pore volume of the gel, $Vp$, was defined as the difference between the elution volume of $D_2O$ and T-2000. The elution volume of T-2000 was defined as the interstitial (or void) volume, $Vi$. So that, the solid (gel) phase volume, $Vs$, was given by the equation $Vs = V - Vi$, where $V$ is the empty column volume. Therefore the elution volume of a sample, $Ve$, can be described by the equation $Ve = Vi + KVp$, where $K$ is the distribution coefficient and shows the degree of solute distribution in gels.

On the basis of the above theory, the porosity, $P$, and the pore volume, $Vsp$, of the gel are determined by the following equation.

$$P = (Vd - Vi)/(V - Vi) = Vp/Vs \ (\%)$$

$$Vsp = PVs/W = Vp/W \ (\text{mL/g})$$

The pore size distribution was estimated by the relationship between pore radius and distribution coefficient on the basis of calibration curve.

## RESULTS AND DISCUSSION

### Preparation of Poly-APR Particles by Inverse Suspension Polymerization

APR dissolves easily in water rather than in organic solvents at 20°C. Accordingly, the preparation of spherical particles of poly-APR in the presence of water as a diluent was examined by means of an inverse suspension polymerization.

The inverse suspension polymerization of water-soluble monomer has been much less studied[5-7] than the normal suspension polymerization of water-insoluble monomer. Especially, with respect to thermo-sensitive polymers, the preparation of spherical gel by a suspension polymerization has been little reported.

Organic solvents which do not dissolve APR and have strong interfacial tension with the aqueous monomer solution are suitable as a dispersion solvent of the inverse suspension polymerization. To obtain a good dispersibility, a difference in specific gravity between organic solvent and aqueous monomer solution should be small.

Table II shows the solubility of APR in various organic solvents. APR completely dissolves in benzene, toluene, and carbontetrachloride but partially dis-

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TABLE I
Molecular Weights and Radii of Equivalent Spheres of the Samples
Used to Determine Calibration Curve[4]

| Sample | Mw | Radius of equivalent spheres $r$ (Å) | Concentration of aq. soln. (wt %) |
|---|---|---|---|
| T-2000[a] | 2,000,000 | 290 | 0.2 |
| T-500[a] | 520,000 | 165 | 0.2 |
| T-250[a] | 250,000 | 114 | 0.2 |
| T-70[a] | 70,800 | 64 | 0.2 |
| T-40[a] | 39,400 | 49 | 0.2 |
| PEG8000[b] | 8,000 | 25.8 | 0.2 |
| PEG3400[b] | 3,400 | 16.7 | 0.2 |
| PEG1500[b] | 1,500 | 11.0 | 0.2 |
| PEG1000[b] | 1,000 | 8.9 | 0.2 |
| PEG600[b] | 600 | 6.9 | 0.2 |
| PEG300[b] | 300 | 4.8 | 0.2 |
| TEG[c] | 150 | 3.4 | 0.5 |
| DEG[d] | 106 | 2.9 | 0.5 |
| EG[e] | 62 | 2.2 | 0.5 |
| D$_2$O[f] | 20 | 1.75 | 0.5 |

[a] Dextran.
[b] Polyethylene glycol.
[c] Triethylene glycol.
[d] Diethylene glycol.
[e] Ethylene glycol.
[f] Heavy water.

solves in cyclohexane, n-hydrocarbon, and 2,2,4-trimethylpentane (iso-octane). Table II indicates that n-hexane, n-heptane, and iso-octane are suitable as a dispersion solvent for the inverse suspension polymerization. But, these solvents have low specific gravity, compared with that of APR (1.043 at 20°C). Therefore the dispersibility was improved by adding carbontetrachloride in dispersion solvent to adjust specific gravity. However, addition of excess amount of carbontetrachloride was not favorable for the polymerization, because of high solubility of APR in carbontetrachloride.

In order to improve the dispersibility and the stability of monomer droplets, dispersing agents of water-in-oil type are usually applied for the inverse suspension polymerization. The dispersing agent of cation type is undesirable, because it forms redox system with peroxide in catalyst.

Sorbitan monooleate (HLB 4.3), sorbitan sesquioleate (HLB 2.8–3.6), fatty acid alkanolamide (HLB 8), poly(ester-ether-ester) (HLB 5–6), and poly(octadecene-co-maleic anhydride) (HLB 5–6, Mw = 50,000) were tested as dispersing agents. Polymerization of APR by the inverse suspension polymerization was carried out under the following conditions; concentration of monomer in aqueous solution was 20 wt %, degree of crosslinking was 10 mol %, volume ratio of n-heptane to aqueous monomer solution was 4 (v/v). The stability of dispersed droplets and the shape of synthesized gels were investigated. Sorbitan monooleate, sorbitan sesquioleate, and poly-(octadecene-co-

TABLE II

Characteristics of Organic Solvents and Solubilities of APR in Organic Solvents

| Organic solvent | b.p.[a] (°C) | s.g.[b] | Interfacial[c] tension (dyn/cm) | Solubility[c] (g/100 mL) |
|---|---|---|---|---|
| n-Pentane | 36.07 | 0.63 | 50.2 | 0.919 |
| n-Hexane | 68.74 | 0.66 | 51.1 | 0.909 |
| n-Heptane | 98.43 | 0.68 | 50.2 | 0.909 |
| n-Octane | 125.67 | 0.70 | 50.8 | 1.082 |
| n-Decane | 174.12 | 0.73 | 51.2 | 1.160 |
| Cyclohexane | 80.74 | 0.78 | 51.4 | 1.343 |
| iso-Octane[d] | 99.24 | 0.69 | 50.0 | 0.742 |
| Benzene | 80.10 | 0.88 | 35.4 | > 4.0 |
| Toluene | 110.63 | 0.87 | 35.7 | > 4.0 |
| CCl$_4$[e] | 76.74 | 1.59 | 43.8 | > 4.0 |

[a] Boiling point.
[b] Specific gravity.
[c] Measured at 20°C.
[d] 2,2,4-Trimethylpentane.
[e] Carbontetrachloride.

maleic anhydride) were satisfactory as dispersing agents. In case of the other dispersing agents, polymerization mixture was emulsified.

These results are summarized as dispersing agents with HLB 3–5 are suitable for the inverse suspension polymerization. Polymeric dispersing agents, which are adsorbed or fixed on the surface of the particles to form solvation layer, seem better than smaller molecular dispersing agents for this polymerization, especially at high monomer concentration range, because the difference of polarity between medium and particle becomes small.

From the above results, n-heptane-carbontetrachloride mixture (5 : 3 (v/v), $d$ = 1.03 (20°C)) as dispersion medium and poly(octadecene-co-maleic anhydride) as dispersing agent were selected for further investigation.

Redox initiator system of APS as water-soluble peroxide and TMEDA as reducing agent, which can initiate polymerization at low temperature, was used for the polymerization. Table III shows optimum amount of initiator to prepare polymer particles with various degrees of crosslinking under various concentrations of monomer on the basis of the yield and the shape of synthesized gels. In this table, the polymer particles were represented such as AR-50-1 and AR-20-10. The first and second numbers in the abbreviation represent the concentration of monomer in aqueous solution and the mol percent of crosslinking agent in feed at polymerization, respectively.

At higher degree of crosslinking, molar ratio of APS to TMEDA had to be increased to some extent, keeping APS concentration constant at 1.0 wt % in monomer (AR-50-1, 5, 10, 15, 20). This result is considered due to the lower reactivity of MBA than that of APR on polymerization. At higher concentration of monomer, amount of APS had to be decreased in the range of 1.5 to 0.6% in monomer, keeping molar ratio of APS to TMEDA constant (1 : 3) (AR-20, 40, 60, 80). This result is considered due to the higher initiation efficiency at higher monomer concentration. The yield of synthesized gels under these conditions was above 95%.

TABLE III
Conditions for Preparation of Gels

| Gel | Concentration of monomer in aq. soln. (wt %) | Degree of crosslinking (mol %) | Initiator | |
|---|---|---|---|---|
| | | | APS[a] (wt %) | APS[a] : TMEDA[b] (mol ratio) |
| AR-50-1 | 50 | 1 | 1.00 | 1 : 2.5 |
| AR-50-5 | 50 | 5 | 1.00 | 1 : 3.0 |
| AR-50-10 | 50 | 10 | 1.00 | 1 : 3.0 |
| AR-50-15 | 50 | 15 | 1.00 | 1 : 3.4 |
| AR-50-20 | 50 | 20 | 1.00 | 1 : 3.6 |
| AR-20-10 | 20 | 10 | 1.50 | 1 : 3.0 |
| AR-40-10 | 40 | 10 | 1.00 | 1 : 3.0 |
| AR-60-10 | 60 | 10 | 0.80 | 1 : 3.0 |
| AR-80-10 | 80 | 10 | 0.60 | 1 : 3.0 |

Dispersion medium: n-Heptane/Carbontetrachloride = 5/3 (v/v).
Weight ratio of monomer phase/dispersion medium: 1/10.
Dispersing agent: 0.125 wt % (to dispersion medium).
Polymerization: 20°C, 2 h, 20 rpm.
[a] Ammonium peroxydisulfate.
[b] N,N,N',N'-Tetramethylethylenediamine.

## Particle Size Distribution

Particle size distribution was measured by sieving, in order to investigate the relationship between particle size and stirring speed. Stirring speed was changed at 200, 350, and 500 rpm under the conditions of constant volume ratio of dispersion medium to monomer phase, 10 (v/v), and constant dispersing agent concentration on dispersion medium, 0.125 wt % (Figure 1). Particle size decreased at higher stirring speed. Effective particle sizes were 145, 80, and 23 $\mu$m for 200, 350, and 500 rpm, respectively. Homogeneity factor became larger and particle size distribution deviated from normal distribution at higher stirring speed. By controlling the stirring speed, the spherical gels with average particle size of 50–500 $\mu$m were easily obtained. Particle size distribution became slightly narrow and particle size became slightly small with increasing the amount of dispersing agent from 0.05 to 0.25 wt % in dispersion medium at 200 rpm of stirring speed.

## Swelling

Swelling volume of spherical gels (177–210 $\mu$m in diameter) with various degrees of crosslinking was measured in water at various temperatures (Figure 2). The swelling volume continuously decreased with increasing temperature, but it leveled off above 50°C and the gels apparently changed from transparent to opaque. This phenomenon was reversible and did not show any hysteresis. This thermo-sensitive property of the gels is considered due to the reversible change of hydrophobicity of the gels with temperature. The change of swelling volume was remarkable with the gels of low degree of crosslinking. But, highly cross-linked gel, which did not show swelling-shrinkage phenomenon, also became opaque above 50°C, showing that hydrophobicity was still changing with
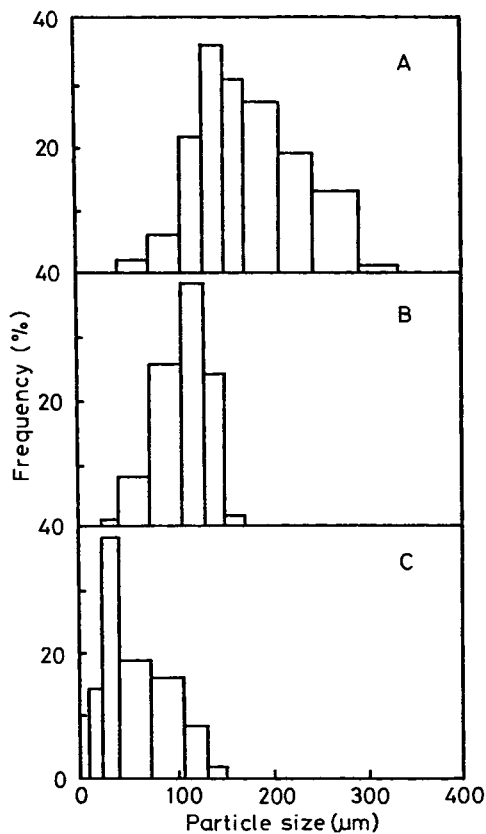
Fig. 1.  Variation of particle size distribution with stirring speed for AR-50-10: (A) 200 rpm; (B) 350 rpm; (C) 500 rpm.
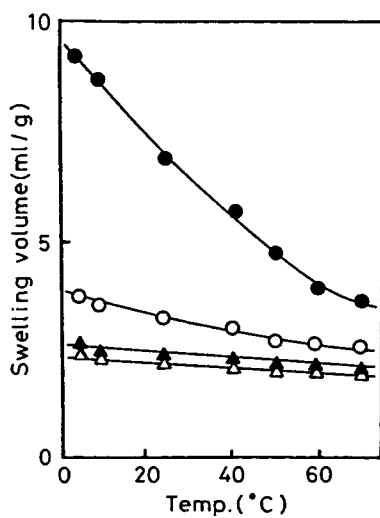


Fig. 2.  Effect of crosslinking on swelling volume at various temperatures: (●) AR-50-1; (○) AR-50-5; (▲) AR-50-10; (△) AR-50-15.

temperature. The change of hydrophobicity can be attributed to the change of
the strength of hydrogen bonding between amide group and water caused by
thermal disturbance of water.

The swelling-shrinkage phenomenon was remarkable with the gels obtained
at low monomer concentration and at low degree of crosslinking (Figure 3).
The swelling ratio was affected by the monomer concentration as well as by
the amount of crosslinking agent.

In order to investigate swelling in organic solvents, the swelling volume in
the mixture of water and ethanol was measured at various mixing ratios (Figure
4). The effect of temperature on the swelling-shrinkage phenomenon became
less at higher content of ethanol and this phenomenon became slight in pure
ethanol. In the presence of ethanol the gels was transparent even above 50°C.

The degree of swelling in various organic solvents was determined (Table
IV). The degree of swelling in alcohols was higher than that in water, but in
the other organic solvents the degree of swelling was lower than that in water.
However, AR-50-1 swelled about three and half times of dried polymer particle
in n-heptane which is nonpolar solvent, showing that the gels have both hy-
drophobicity and hydrophilicity. The effect of temperature on the change of
hydrophobicity was not observed in organic solvents.

## Pore Structure of Gel

In order to investigate the pore structure of the gels in swelling state, the
pore volume, the porosity, and the pore size distribution were estimated from
calibration curves obtained by aqueous size exclusion chromatography (Table
V, Figures 5, 6, 7).

The results on AR-50-5, -10, -15, and -20 show that the molecular weight at
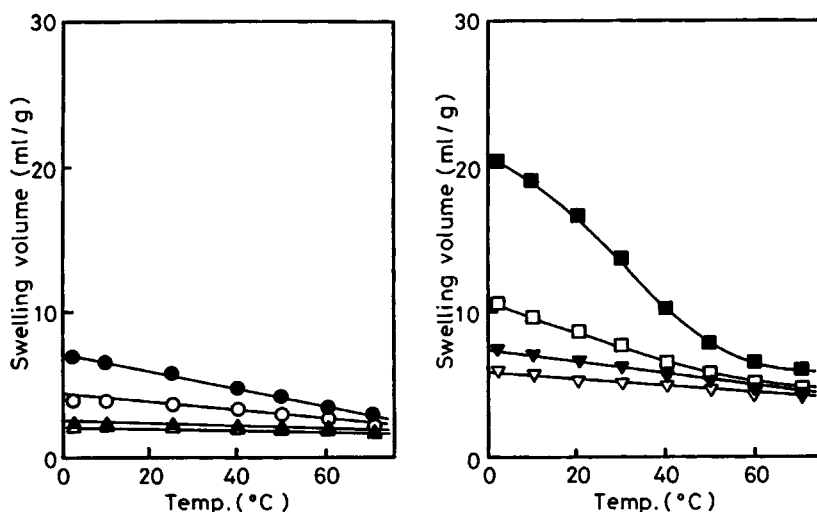exclusion limit of the gels was about 1,500 irrespective of the degree of cross-



Fig. 3.   Swelling volume at various temperatures of gels prepared at various monomer concen-
tration: (●) AR-20-10; (○) AR-40-10; (▲) AR-60-10; (△) AR-80-10; (■) AR-20-1; (□) AR-40-1;
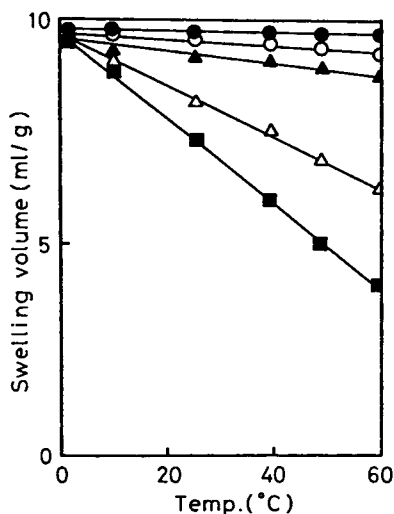(▼) AR-60-1; (▽) AR-80-1.

Fig. 4.  Dependence of swelling volume of AR-50-1 on ethanol content in ethanol-water mixture at various temperatures: (●) 100%; (○) 75%; (▲) 50%; (△) 25%; (■) 0%.

linking, and the porosity and the pore volume decreased with the increase of crosslinking in the range from 62 to 53% and in the range from 1.3 to 0.8 mL/g, respectively (Table V). Kuga[4] reported the molecular weights and radii of equivalent spheres $(r)$ of some polymers. On the other hand, Halasz et al.[8] found that the rotational coil diameters of polystyrenes must be about 2.5 times smaller than the diameters of the pores in the solid (i.e., $\emptyset$ values) to allow the polymer unhindered access to the pores. In addition, Crispin et al.[9] found that the $\emptyset/2r$ ratios of dextrans vary between 2.5 (for T-500) and 3.2 (for T-70). From these references[4,8,9] and our experimental results (Fig. 5), the radii of the pores in these poly-APR were estimated to be smaller than 30 Å. Also it was found that the mean pore radius of the gels decreased very slightly with an increase in crosslinking.

When the monomer concentration at polymerization was increased from 20 to 80 wt %, keeping the degree of crosslinking constant (10 mol %), the molecular weight at exclusion limit decreased from about 20,000 to about 600. Thus the radius of the largest pore in the AR-20-10 was estimated to be about 100 Å and the portion of large pore disappeared in the gels prepared with higher concentration of monomer. The porosity and the pore volume decreased from 83 to 52% and from 2.3 to 0.8 mL/g, respectively, with increasing monomer concentration (Table V, Fig. 6). The pore structure of the gel in swelling state is affected by the amount of crosslinking agent and by the monomer concentration. This indicates the water used as a diluent plays a major role to determine the pore structure of the gels. But, the effect of the monomer concentration saturates at very high monomer concentration range (comparison of AR-60-10 and AR-80-10).

The effect of temperature on the pore structure was investigated by using AR-20-10 which had high thermo-sensitivity (Table V, Fig. 7). The interstitial volume decreased significantly by lowering the column temperature, resulting in high degree of packing, because of the higher swelling volume of the gels at

TABLE IV
Swelling Ratio of Gels in Water and Organic Solvents

Swelling ratio[a]

| Gel | Degree of crosslinking (mol %) | H$_2$O | | | MeOH[b] | | | EtOH[c] | | | Acetone | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1°C | 25°C | 40°C | 1°C | 25°C | 40°C | 1°C | 25°C | 40°C | 1°C | 25°C | 40°C |
| AR-50-1 | 1 | 5.94 | 4.43 | 3.69 | 5.95 | 5.83 | 5.51 | 6.03 | 5.85 | 5.79 | 4.34 | 4.19 | 3.96 |
| AR-50-5 | 5 | 2.46 | 2.15 | 1.96 | 2.94 | 2.26 | 2.20 | 2.29 | 2.27 | 2.18 | 1.84 | 1.76 | 1.72 |
| AR-50-10 | 10 | 1.82 | 1.61 | 1.56 | 1.71 | 1.70 | 1.68 | 1.71 | 1.70 | 1.67 | 1.38 | 1.35 | 1.33 |
| AR-50-15 | 15 | 1.64 | 1.49 | 1.44 | 1.58 | 1.57 | 1.52 | 1.57 | 1.56 | 1.51 | 1.35 | 1.32 | 1.26 |
| AR-50-20 | 20 | 1.60 | 1.48 | 1.46 | 1.59 | 1.58 | 1.57 | 1.58 | 1.57 | 1.57 | 1.40 | 1.37 | 1.36 |

Swelling ratio[a]

| Gel | Degree of crosslinking (mol %) | DMF[d] | | | Dioxane | | | n-Heptane | | | EtOAc[e] | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 1°C | 25°C | 40°C | 1°C | 25°C | 40°C | 1°C | 25°C | 40°C | 1°C | 25°C | 40°C |
| AR-50-1 | 1 | 4.20 | 3.98 | 3.96 | 4.44 | 4.42 | 4.42 | 3.58 | 3.52 | 3.47 | 3.53 | 3.41 | 3.35 |
| AR-50-5 | 5 | 1.84 | 1.76 | 1.72 | 1.91 | 1.88 | 1.87 | 1.44 | 1.40 | 1.38 | 1.35 | 1.34 | 1.34 |
| AR-50-10 | 10 | 1.49 | 1.46 | 1.44 | 1.48 | 1.44 | 1.44 | 1.26 | 1.22 | 1.19 | 1.23 | 1.22 | 1.22 |
| AR-50-15 | 15 | 1.41 | 1.38 | 1.36 | 1.38 | 1.36 | 1.35 | 1.21 | 1.17 | 1.12 | 1.19 | 1.17 | 1.16 |
| AR-50-20 | 20 | 1.47 | 1.46 | 1.46 | 1.45 | 1.43 | 1.43 | 1.30 | 1.28 | 1.23 | 1.28 | 1.24 | 1.22 |

[a] Swelling ratio = wet volume (mL)/Dry volume (mL), [b]Methanol, [c]Ethanol, [d]N,N-Dimethylformamide, [e]Ethoxyacetic acid.

TABLE V
Pore Structure of Gels Determined by Size Exclusion Method

| Gel | Measured temp. (°C) | $M_{lim}$ [a] | Porosity (%) | Pore volume (mL/g) |
|---|---|---|---|---|
| AR-50-5 | 20 | 1,500 | 62.2 | 1.32 |
| AR-50-10 | 20 | 1,500 | 55.8 | 0.92 |
| AR-50-15 | 20 | 1,500 | 53.0 | 0.73 |
| AR-50-20 | 20 | 1,500 | 58.3 | 0.78 |
| AR-20-10 | 20 | 20,000 | 83.4 | 2.29 |
| AR-40-10 | 20 | 6,000 | 63.0 | 1.08 |
| AR-60-10 | 20 | 800 | 58.8 | 0.89 |
| AR-80-10 | 20 | 600 | 52.3 | 0.77 |
| AR-20-10 | 10 | 20,000 | 89.8 | 2.64 |
| AR-20-10 | 20 | 20,000 | 85.7 | 2.30 |
| AR-20-10 | 35 | 20,000 | 83.9 | 2.08 |
| AR-20-10 | 50 | 20,000 | 76.2 | 1.65 |

[a] Molecular weight at exclusion limit.

lower temperature. The molecular weight at exclusion limit did not change with temperature, but the porosity and the pore volume decreased at higher temperature. Mean pore radius decreased slightly by lowering the temperature, corresponding to the expansion of polymer molecules by hydration.

## CONCLUSIONS

Inverse suspension polymerization of cross-linked poly-APR was investigated in order to synthesize thermo-sensitive spherical gels. Mixed solvent system
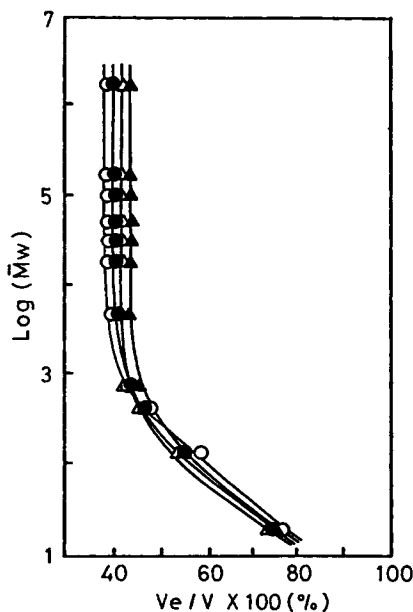


Fig. 5. Effect of degree of crosslinking on calibration curves of gels at 20°C: (●) AR-50-5; (○) AR-50-10; (▲) AR-50-15; (△) AR-50-20.
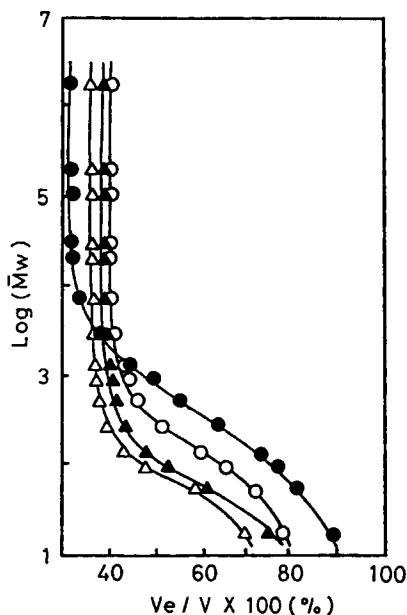
Fig. 6. Effect of monomer concentration on calibration curves of gels at 20°C: (●) AR-20-10; (○) AR-40-10; (▲) AR-60-10; (△) AR-80-10.

of n-heptane (or n-hexane, iso-octane) and carbontetrachloride was selected as dispersion medium and poly-(octadecene-co-maleic anhydride) as dispersing agent. Fine spherical gels with 50–500 μm of particle size were obtained in high yield of at least 95%.

The swelling volume of the gels was high both in water and alcohols. But, the gels swelled even in nonpolar organic solvents, showing that the gels have both hydrophobic and hydrophilic properties. The swelling volume of the gels in water continually decreased by raising temperature and continually increased by lowering temperature. This thermo-sensitive property of the gels can be attributed to the change of the hydrophobicity of the gels resulting from the change of the strength of hydrogen bonding by amide group with temperature. The dependence of swelling ratio on temperature increased with decreasing the degree of crosslinking or with decreasing the monomer concentration at polymerization.

The pore radius of the gels (synthesized at 50% monomer concentration) was smaller than 30 Å. With increasing the degree of crosslinking from 5 to 20 mol %, the porosity and the pore volume decreased from 62 to 53% and from 1.3 to 0.8 mL/g, respectively, but the mean pore radius changed little. However, with increasing the monomer concentration at polymerization, the pore size distribution became narrow, the mean pore radius became small, and large pores disappeared. The porosity and the pore volume decreased from 83 to 52% and from 2.3 to 0.8 mL/g, respectively, with increasing the monomer concentration from 20 to 80 wt %. The pore structure of the gels in swelling state was affected by the amount of crosslinking agent and by the monomer concentration. Especially, the water used as the diluent seems to act as a porogenic agent in analogy with the diluent in describing the preparation of macroporous styrene-
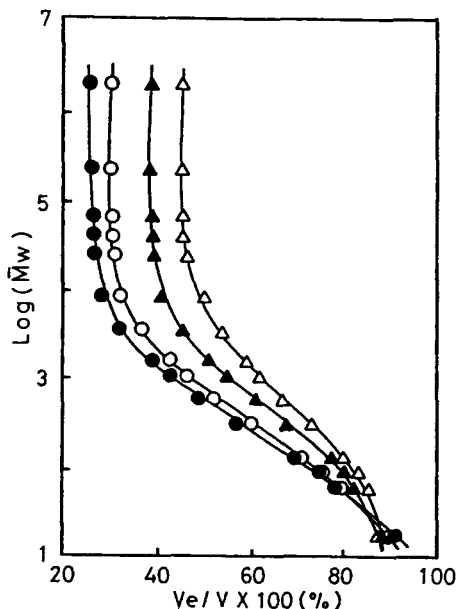
Fig. 7. Effect of column temperature on calibration curves of AR-20-10: (●) 10°C; (○) 20°C; (▲) 35°C; (△) 50°C.

divinylbenzene copolymers. The hydrophobicity of the gels changes with temperature even at high degree of crosslinking, i.e., hard gels also have thermosensitive property, although they do not show any marked swelling-shrinkage response to temperature. Thermo-sensitive adsorbents or separation gels, which can be used, e.g., in a way of loading at high temperature and elution at low temperature, are considered possible to be developed, and they are now under investigation.

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