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Influence of graft copolymer structure on the dimensions and morphology of core–corona type microgels

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Several types of poly(vinyl chloride)-*graft*-poly(α-methylstyrene) (P(VC-*g*-MeSt)) graft copolymers whose branch numbers and branch lengths are different, were crosslinked with a dianionic dimer of 1,1-diphenylethylene in a mixed solvent of tetrahydrofuran (good solvent for PVC and PMeSt) and cyclohexane (non-solvent for PVC). The crosslinked products were characterized using gel permeation chromatography and electron microscopy. A microphased core–corona type microgel was synthesized when the graft copolymer has a small number of long branches. The size distribution of the crosslinked products became broad with increase in the branch number of the graft copolymer. The average number of graft copolymers per microphased core–corona type microgel was calculated from the electron micrographs to be 12.5.

(Keywords: poly(vinyl chloride)-*graft*-poly(α-methylstyrene); selective solvent; micelle; crosslinking; core–corona type microgel)

INTRODUCTION

When graft or block copolymers are dissolved in a selective solvent for one block, they aggregate to form micelles which consist of a compact core of insoluble blocks surrounded by solvated blocks, and the solvated blocks prevent macroscopic flocculation of the copolymers[1–3]. If the core is crosslinked in this state, macrogelation caused by inter-core crosslinking might be prevented because the outer solvated blocks protect the inner core. The crosslinked product is expected to be a core–corona type microgel. We have actually obtained a microphased core–corona type microgel by crosslinking of a graft copolymer in a selective solvent for the branch polymer[4], and other workers have also reported the crosslinking of micelles[5–7]. However, these reports did not discuss the factors that influence the dimensions and morphology of the core–corona type microgel. The dimensions and morphology of a core–corona type microgel are considered to depend mainly on the dimensions and structure of the micelles, and the latter is also strongly affected by copolymer structure, solvent conditions and temperature. Noolandi *et al.*[8] deduced from their model that micelle dimensions increase with increasing fraction of insoluble block and degree of polymerization of the copolymer. Candau *et al.*[9] reported that a graft copolymer with a low content of soluble block forms a compact and more aggregated micelle. Various results showing that the structure of the micelles is drastically affected by the structure of the copolymer have also been reported[10–14]. With these results in mind, we synthesized several types of poly(vinyl chloride)-*graft*-poly(α-methylstyrene) (P(VC-*g*-MeSt)) copolymers whose branch numbers and lengths are different, and investigated the influence of graft copolymer structure on the dimensions and morphology of the core–corona type microgel. Crosslinking was carried out in a mixed solvent of tetrahydrofuran (THF), a good solvent for both PVC and PMeSt, and cyclohexane (CH), a non-solvent for PVC, by using a dianionic dimer of 1,1-diphenylethylene as crosslinking agent. The size distribution of the crosslinked products was observed using gel permeation chromatography (g.p.c.). Electron microscopic observation was used to clarify the structure of the products.

EXPERIMENTAL

Preparation of P(VC-g-MeSt)

The PVC used in this work is one fractionated by a THF–water solvent–non-solvent system. P(VC-*g*-MeSt) was prepared by a condensation reaction between PVC and a lithiated PMeSt which was prepared by polymerization of α-methylstyrene with butyllithium initiator in toluene under vacuum. Before the condensation reaction, the impurities in the PVC/THF solution were eliminated with sodium triphenylmethane by adding it to the solution until the unreacted dark-red colour of sodium triphenylmethane remains stable for a few seconds. Then the purified PVC solution was reacted with lithiated PMeSt/toluene at −78°C until the red colour of lithiated PMeSt disappeared completely. All the operations were carried out in a high-vacuum system. The reaction products were poured into methanol; the precipitates were filtered and then dried. PVC and PMeSt homopolymer in the reaction products were extracted with a THF–methanol mixed solvent and cyclohexane, respectively. The composition of the graft copolymer was determined by proton n.m.r. spectroscopy (Hitachi R-24B High Resolution NMR Spectrometer). The molecular weight of the polymers was determined by the universal calibration method of gel permeation chromatography[15]. The characteristics of the graft copolymers are summarized in *Table 1*.

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Table 1 Characteristics of graft copolymers

No.	Molecular weight, $M_n (\times 10^{-4})$ PVC	PMeSt	Number of branches (per PVC)	Amount of PMeSt (wt%)
G1-1	5.9	1.2	1.5	23
G1-2	5.9	1.8	1.5	31
G1-3	5.9	2.5	1.6	40
G1-4	5.9	3.5	1.8	52
G2	6.5	0.4	7.8	32
G3	6.9	1.8	4.5	54
G4	8.3	0.27	32	51

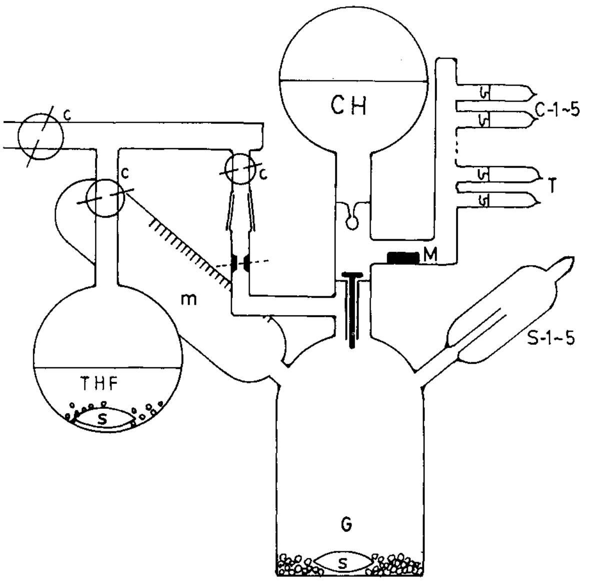

Figure 1 Apparatus for crosslinking reaction: G, graft copolymer; M, magnetic hammer; CH, cyclohexane; T, sodium triphenylmethane/THF; C, crosslinking agent; S, sampling ampoules; m, ampoule to measure the volume of the solution; s, stirrer; c, stopcocks

Preparation of crosslinking agent

A dianionic dimer of 1,1-diphenylethylene was used as crosslinking agent in this work. Preparation of the crosslinking agent was carried out in a high-vacuum atmosphere using glass apparatus equipped with breakseals[16,17]. The 1,1-diphenylethylene in THF was reacted with a sodium mirror overnight and then filtered through a sintered-glass disc into the storage vessel. One portion of the crosslinking agent was deactivated with methanol; and the reacted one was characterized by ^{1}H n.m.r. (Hitachi R-24B High Resolution NMR Spectrometer). The ratio of integrated values of aliphatic hydrogen (chemical shift 1.8 ppm) and aromatic hydrogen (chemical shift 7.1 ppm) is 1/5, so the structure of the crosslinking agent is regarded as a dimer.

Crosslinking reaction

The apparatus used for the crosslinking reaction is shown in *Figure 1*. Before crosslinking, impurities in the graft copolymer solution were eliminated with sodium triphenylmethane T by the same method as in graft copolymer preparation. One ampoule of crosslinking agent C-1~5 was introduced into the purified graft copolymer solution with agitation, and one portion of the crosslinked product was transferred to a sampling ampoule S-1. These operations were repeated several times. All the reactions were carried out under high vacuum. The crosslinking reaction conditions of the graft copolymers are as follows: concentration of polymer, 1 g dl^{-1}; cyclohexane content, 80 vol%; temperature, 25°C. The crosslink density of the reacted product was calculated from the amount of NaCl, the product of the condensation reaction between carbanions and vinyl chloride units (determined by Volhard's titration method). G.p.c. was done using an HLC-802A (Toyo Soda) apparatus: column, GMH 6; flow rate, 1 ml min^{-1}; temperature, 38°C; solvent, THF; polymer concentration, 0.5 g dl^{-1}. Transmission electron microscopic observation was carried out with an Hitachi HS-7 Electron Microscope. The PMeSt part was stained using ruthenium tetraoxide (RuO_4). A shadowed sample, prepared by shadowing with palladium after staining with RuO_4, was also observed. The turbidity behaviour of graft copolymers under various solvent conditions was observed using a spectrophotometer (Hitachi Perkin–Elmer 135 UV-VIS Spectrophotometer) at 450 nm.

RESULTS AND DISCUSSION

Turbidity of graft copolymer

In order to investigate the solvent conditions for micellization and the stability of the micelle formed, a turbidimetric titration of graft copolymers was carried out at various CH/THF ratios. *Figure 2* shows two typical types of turbidity behaviour of PVC and graft copolymer G1-4. In the case of PVC, high turbidity appears at 58 vol% CH, and then precipitation occurs with further addition of CH to this solution. In contrast to PVC, the transmittance of the G1-4 graft copolymer system decreases within the range 67–75 vol% CH, and then shows a constant value with further increase of CH. Above 67 vol% CH the solution had a bluish tint (characteristic of micelles) and was stable on prolonged storage for many weeks. The results of turbidimetric titrations of graft copolymers are given in *Table 2*. Graft copolymer G1-1 shows a similar turbidity behaviour to PVC and was precipitated at 65 vol% CH. G1-2 shows a high turbidity at 56–70 vol% CH, and then precipitation also occurred a few hours later. A translucent milky opalescence was observed in the G1-3 system above 60 vol% CH and was stable on prolonged storage. In contrast to these graft copolymers with low branch content, graft copolymers G1-4, G3 and G4 with high branch content showed a bluish tint and were stable on prolonged storage. Graft copolymer G2, whose branch

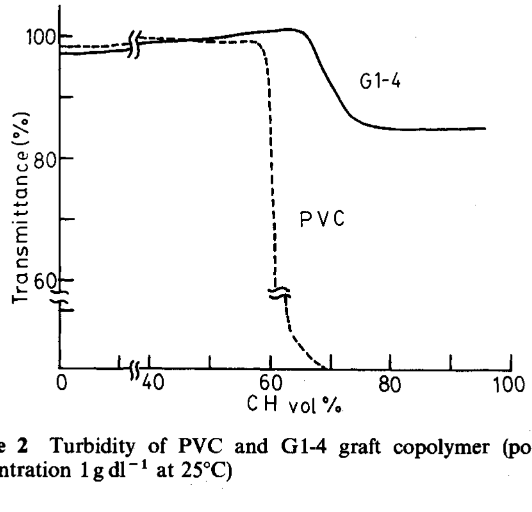

Figure 2 Turbidity of PVC and G1-4 graft copolymer (polymer concentration 1 g dl^{-1} at 25°C)

Table 2 Turbidity behaviour of graft copolymers

No.	Increasing region of turbidity (vol% of CH)	Amount of PMeSt (wt%)	Apparent feature of graft copolymer in high vol% of CH
PVC	58–66	0	Precipitation
G1-1	55–65	23	Precipitation
G1-2	56–70	31	Precipitation
G1-3	59–76	40	Translucent milky opalescence
G1-4	67–76	52	Bluish tint
G2	66–77	32	Bluish tint
G3	67–76	54	Bluish tint
G4	68–77	51	Bluish tint

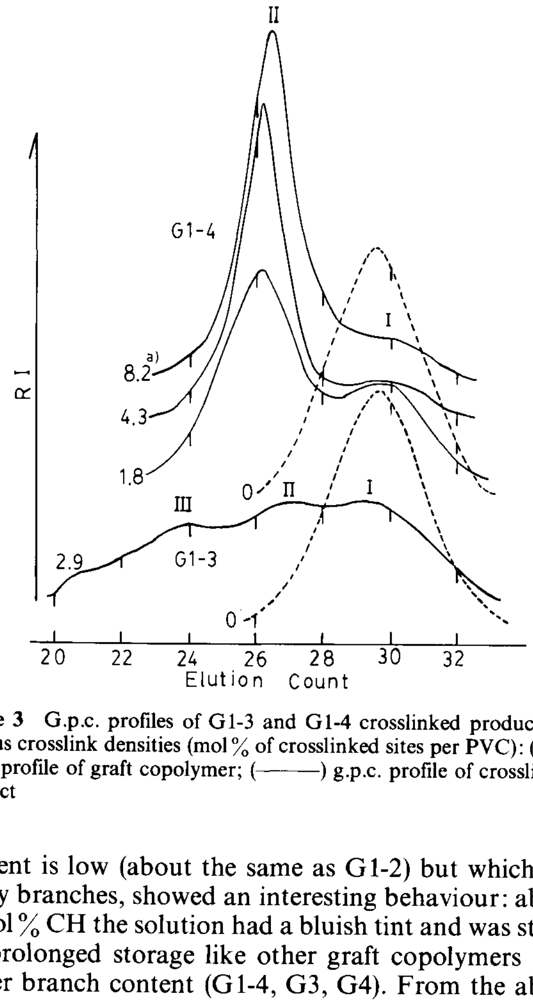

Figure 3 G.p.c. profiles of G1-3 and G1-4 crosslinked products, at various crosslink densities (mol% of crosslinked sites per PVC): (– – –) g.p.c. profile of graft copolymer; (———) g.p.c. profile of crosslinked product

content is low (about the same as G1-2) but which has many branches, showed an interesting behaviour: above 68 vol% CH the solution had a bluish tint and was stable on prolonged storage like other graft copolymers with larger branch content (G1-4, G3, G4). From the above results, it is expected that a large particle or an unstable macro-emulsion are formed in the systems of G1-1, G1-2 and G1-3, and that stable micelles are formed in the G1-4, G3, G4 and G2 graft copolymer systems. The above behaviour will be discussed in a later section in connection with g.p.c. profiles and electron micrographs of crosslinked products.

G.p.c. profiles of crosslinked products

Effect of branch content. G.p.c. profiles of G1-3 and G1-4 crosslinked products are shown in *Figure 3*. Because the stock solutions of G1-1, G1-2 and G1-3 (above crosslink density 4.6 mol%) did not pass through the membrane filter (pore size 0.45 μm) of g.p.c., we could not run g.p.c. The characteristic features of g.p.c. profiles are as follows. G1-3 shows three peaks which are considered microgels of monomers (peak I), micelles (peak II) and large particles (peak III). All the g.p.c. profiles of G1-4 crosslinked products show two peaks of microgels corresponding to monomers (peak I) and micelles (peak II). A new peak in the elution count region lower than peak II is not observed even in more highly crosslinked products. From the above results, we can deduce the following conclusions. Graft copolymers with lower branch content (G1-1, G1-2 and G1-3) form unstable micelles or large aggregates, and then macrogelation caused by inter-core crosslinking occurs as crosslinking proceeds. Graft copolymers with higher branch content (G1-4) form stable micelles, and inter-core crosslinking is restrained completely.

These behaviours can be explained by the amount of outer soluble branches in micelles, i.e. if the branch content is low, protection against aggregation between micelles is not good enough. As peak II shifts towards the high elution count region with increasing crosslink density, we can assume that the cores shrink considerably as crosslinking proceeds.

Effect of branch number. Figure 4 shows g.p.c. profiles of crosslinked products of G3 and G4 whose numbers of branches are larger than G1-4. The crosslinked products of G4 whose crosslink densities are more than 3.1 mol% did not pass through the membrane filter for g.p.c. G3 crosslinked products show distinct peaks I and II, like G1-4. From a comparison with g.p.c. profiles of G1-4, G3 and G4 crosslinked products, it can be seen that the halfwidth of peak II becomes broad as the number of branches increases (see *Table 1*). Especially, in the case of G4, peaks I, II and III are not distinguishable. This broad size distribution of graft copolymer micelles has also been observed in other reports[18,19]. A graft copolymer with many short branches can be regarded as a random copolymer. The association behaviour of these copolymers is expected to be very complicated, so it is also expected that the micelle consists of a more or less swollen core, where the insoluble blocks are swollen by soluble blocks, surrounded by a small amount of soluble blocks. From the g.p.c. profile of crosslinked product G4, we expect that the association system is similar to an open association[20,21]. As the top point of peak II in system G3 lies in a higher elution count region than that of system

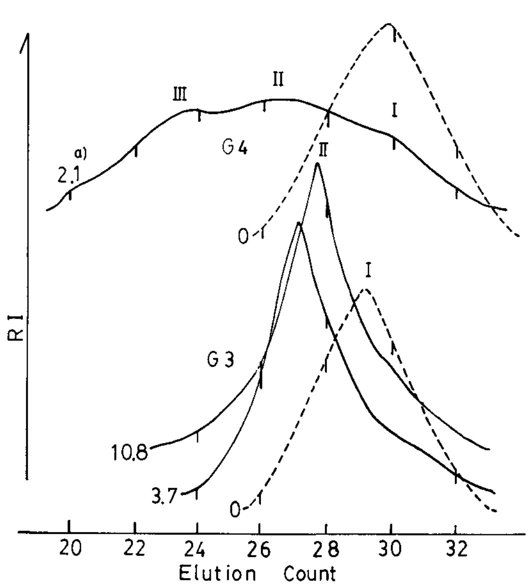

Figure 4 G.p.c. profiles of G3 and G4 crosslinked products, at various crosslink densities: curves as in *Figure 3*

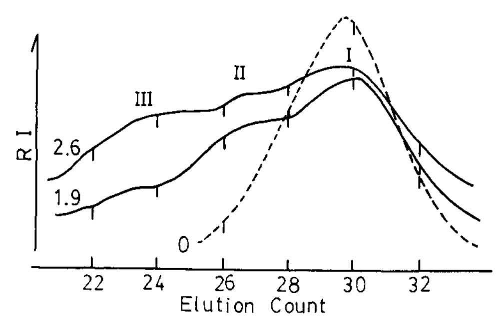

Figure 5 G.p.c. profiles of G2 crosslinked products, at various crosslink densities: curves as in *Figure 3*

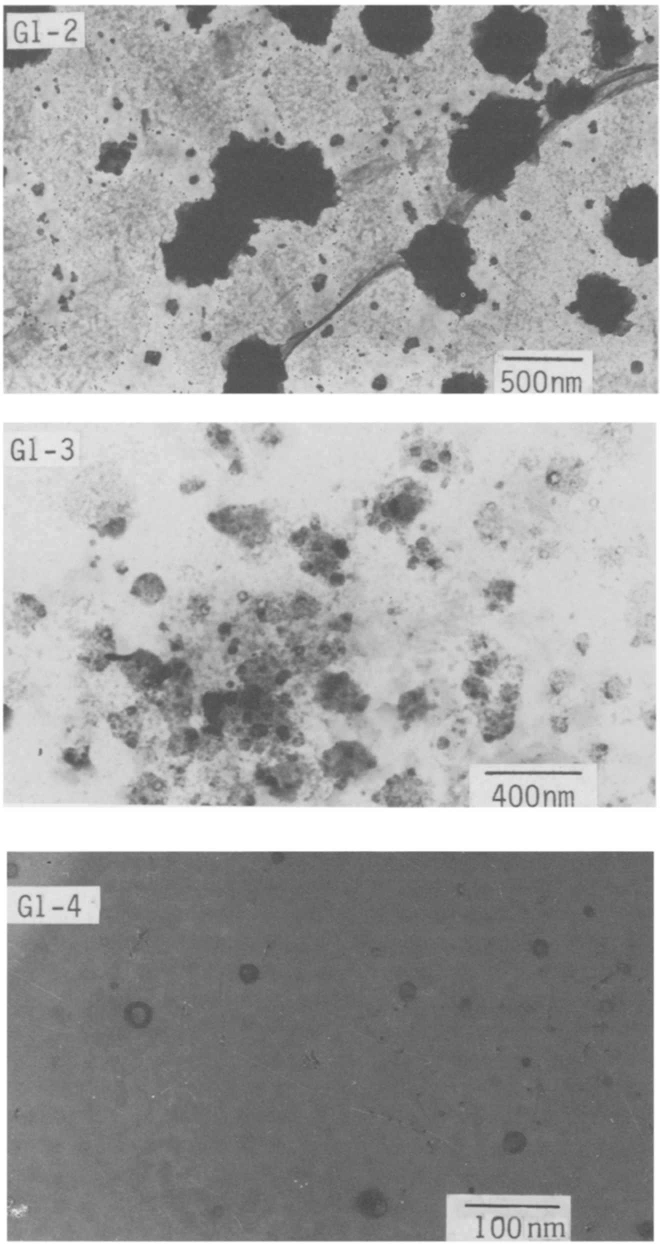

Figure 6 Electron micrographs of G1-2, G1-3 and G1-4 crosslinked products, at crosslink density of 2.7 mol% (G1-2), 2.9 mol% (G1-3) and 4.3 mol% (G1-4)

G1-4 (*Figure 3*), the hydrodynamic volume of a G3 micelle is thought to be smaller than that of a G1-4 micelle.

G.p.c. profiles of G2 crosslinked products, for which the graft copolymer has many short branches and the branch content is low (see *Table 1*), are given in *Figure 5*. Products more highly crosslinked than 3.1 mol% could not be run by g.p.c. Very broad peaks (I, II, III) like those observed in system G4 can be seen, and a new peak appears in the lower elution count region as the crosslink density increases. By considering the above results in connection with the results of turbidity (see *Table 2*: G2 showed a transparent bluish tint although G1-2, for which the branch content is the same as G2, was precipitated in similar solvent conditions), we can deduce that the many branches combined in the backbone hinder the aggregation of the backbone (i.e. precipitation is hindered by many branches) and the association system is open. From the fact that the highly crosslinked products of G2 and G4 graft copolymer (above a crosslink density of about 3 mol%) do not pass through the membrane filter for g.p.c., we suppose that inter-core crosslinking between aggregates occurs.

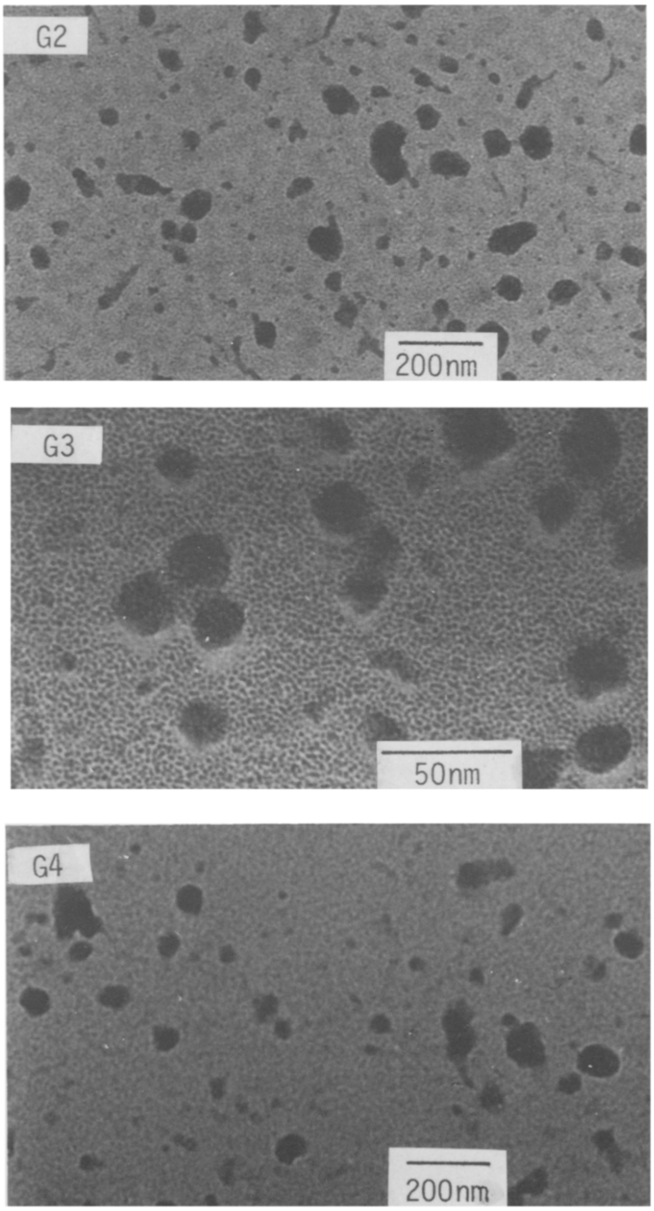

Figure 7 Electron micrographs of G2, G3 and G4 crosslinked products, at crosslink density of 3.1 mol% (G2), 3.7 mol% (G3) and 3.1 mol% (G4). Electron micrograph G3 is of shadow-cast specimen

Electron microscopy

Electron micrographs of crosslinked products for G1-2, G1-3 and G1-4 are given in *Figure 6*. As the branch content of graft copolymers increases, the structure of the crosslinked products changes from a large particle (G1-2) to a microphased core–corona type microgel (G1-4). We can observe the transition typically in the G1-3 system: the crosslinked products contain microphased core–corona type microgels as well as large particles. However, in the case of graft copolymers that have many short branches, the crosslinked products have a broad size distribution and show no microphase-separated structures, as shown in *Figure 7*. From this observation, as mentioned in the previous section, we can also deduce that the core part of the micelle is composed of PVC backbones and some PMeSt branches.

The transmission electron micrograph of G3 crosslinked product is of a shadowed sample (shadowing angle 40°). From this, we find that the microgels have almost spherical structure. From the average volume of microgels, one is able to calculate the molecular weight and association number of the microgels[22]. The molecular weights of G1-4 and G3 microgels are 1.53×10^5 and 1.3×10^5 and the numbers of graft copolymers per microgel are 12.5 and 8.7, respectively.

CONCLUSIONS

In this work, we conclude that a more suitable graft copolymer structure for synthesis of a microphased core–corona type microgel is one with a small number of long branches when the branch content is more than about 40 wt%. We confirm that the size distribution of the microgel is sharpened when the branch number is small. Further studies must be done in order to understand the effects of environment (temperature, solvent conditions, etc.) on the structure.

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