

# Synthesis and Characterization of Nonionic 1-Vinyl-2-pyrrolidinone/Methacryloxy Silicone Copolymers: Effects of Molecular Weight of Silicone and Crosslinking Density

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**ABSTRACT:** Nonionic 1-vinyl-2-pyrrolidinone/methacryloxy silicone copolymers (VP/VS copolymers) were prepared and characterized as functions of molecular weight of silicone and crosslinking density. Fourier transform infrared spectroscopy,  $^{13}\text{C}$ -NMR, and pyrolysis gas chromatography–mass spectrometry study showed that those copolymers were successfully synthesized. Also, the gel-permeation chromatography spectrum exhibited a fairly narrow distribution of the molecular weight of the polymer. It was found that the turbidity in ethanol (EtOH) and the glass-transition temperature of crosslinked VP/VS copolymers are influenced by the amount of crosslinking agent. However, in the case of branched VP/VS copolymers, a transparent solution was obtained, regardless of the molecular weight of silicone. SEM/EDS study revealed that silicone is more abundant on the coating surface than on the interface of coating/glass. This is probably because Si-containing chains have lower surface energy than that of vinylpyrrolidinone-containing chains. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 2244–2253, 2002

**Key words:** silicones; crosslinking; glass transition; X ray

## INTRODUCTION

Silicone-containing polymers have attracted great interest for many years because they have many attractive attributes such as flexibility, low surface tension, excellent electrical properties, good weatherproofing ability, nonflammability, as well as their stability toward heat and chemicals.<sup>1,2</sup> Recently, a wide range of organopolysiloxanes with different structures have been put into practical use in the field of lubricants for cars and machines,<sup>3</sup> extreme-pressure additives,<sup>4</sup> and cosmetics.<sup>5–7</sup>

In the cosmetic area, studies on hair-care products, particularly hair spray, hair mousse, and hair gel, have proceeded rather constantly.<sup>8–13</sup> The features that silicone provide in hair-care usage are optical and esthetic effects such as shine and gloss, and high lubrication with a smooth conditioned feel. Though there are many attractive features of silicones, they also have several limitations. Primary among these is the poor adhesion or substantivity of silicones on hair, which leads to rapid loss through washing and normal wear and poor durability. To address these limitations of silicones, a new class of silicone copolymers has been developed. The polymers combine silicone chemistry with acrylic resin or hard polymer with reactive site, that is, 1-vinyl-2-pyrrolidinone through a process called

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graft copolymerization.<sup>3,14</sup> The copolymer can have overall synergy properties such as the lubricant effect of silicone and the setting property of hard polymers. Because the silicone branches of these graft copolymers are not significantly miscible with the hard polymer segment, these polymers phase separate in dry coatings into a hard polymer segment and the silicone phase.<sup>15–17</sup> This is the reason that the polymers have a duality of advantages.

When the hard polymer segment is so designed as to have a strong substantivity to hair, this provides a mechanism to anchor the surface silicone to the hair. The degree of surface siliconization of such coatings can be determined by dynamic contact angle analysis,<sup>15</sup> an attenuated total reflectance Fourier transform infrared spectroscopic (ATR FTIR) study,<sup>16</sup> electron spectroscopy for chemical analysis (ESCA),<sup>17</sup> and SEM/EDS analysis.<sup>17</sup>

The purpose of the present work is to synthesize VP/VS copolymers as functions of the molecular weight of silicone and the amount of crosslinking agent, and to investigate properties such as turbidity in ethanol (EtOH) and glass-transition temperature ( $T_g$ ). Also, the coating was observed in terms of the surface composition using SEM/EDS technique.

## EXPERIMENTAL

### Materials

Methacryloxy silicones (VS), FM0711 ( $M_w = 1000$ ), FM0721 ( $M_w = 5000$ ), FM0725 ( $M_w = 10,000$ ) are commercially available products (Chisso, Japan). 1-Vinyl-2-pyrrolidinone (VP; Aldrich, Milwaukee, WI), and vinyl-terminated polydimethyl siloxane (SV, viscosity 200 cst; Aldrich) as crosslinking agent were used as supplied. Azobisisobutyronitrile (AIBN; Wako Pure Chemicals, Tokyo, Japan) was used as an initiator and anhydrous EtOH

(Carlo Erba, Milano, Italy) was used as a solvent of solution polymerization. *n*-Hexane (Dae-jung, Korea) was of analytical grade.

### Methods

#### Synthesis of 1-Vinyl-2-pyrrolidinone/Methacryloxy Silicone (VP/VS) Copolymers

Introduced into a 1-L four-neck flask were 380 g of EtOH and the compositions for VP/VS copolymers, listed in Table I, were added to the solvent under a  $N_2$  stream. EtOH (20 g) containing AIBN (1 g; 1 wt % based on the total amount of monomers) was added over 30 min to the flask under mechanical stirring (200 rpm) at refluxing temperature (78°C) and the reaction was continued for 6 h. After the reaction was completed, the resulting opaque polymer was purified by reprecipitation from *n*-hexane, and kept in a vacuum oven until further use.

#### Instrumental Analysis

FTIR (Nicolet 560; Nicolet Instruments, Madison, WI), <sup>13</sup>C-NMR (ARX3000, Avance 400 NMR), and pyrolysis gas chromatography (GC) (HP-5890, column: HP-1)—mass spectrometry (Mass) (5989B) were used for the structure analysis of VP/VS copolymers. Their molecular weights and distributions were determined by GPC with a Waters 600 (column: Styragel HR; Waters Associates, Milford, MA). Differential scanning calorimetry (DSC) experiments were performed on a DuPont model 910 (DuPont, Boston, MA) under  $N_2$  for determining the  $T_g$  of copolymers.

The relative turbidity of EtOH solution of copolymers (5% solid content) was determined by 2100 AN Turbidimeter (Hach Co., Loveland, CO). The samples were prepared by sonicating the copolymer in EtOH.

#### SEM/EDS

To investigate the surface characteristics of VP/VS copolymers, the films were prepared by

**Table I** Composition for 1-Vinyl-2-pyrrolidinone/Methacryloxy Silicone Copolymers

Designation <sup>a</sup>	Exp1-1	Exp2-1	Exp3-1	Exp3-2	Exp3-3	Exp3-4
VP(g)	90	90	90	90	90	90
FM0711(g)	10	—	—	—	—	—
FM0721(g)	—	10	—	—	—	—
FM0725(g)	—	—	10	8	5	—
SV(g)	—	—	—	2	5	10

<sup>a</sup> VP, 1-vinyl-2-pyrrolidinone; FM0711, methacryloxy silicone ( $M_w = 1000$ ); FM0721, methacryloxy silicone ( $M_w = 5000$ ); FM0725, methacryloxy silicone ( $M_w = 10,000$ ); SV, vinyl-terminated polydimethyl siloxane (viscosity, 200 cst).

casting the solution in EtOH (30 wt %) onto a glass and drying in an oven at 70°C for 10 h. After peeling off the film from the glass, the front side (surface of the coating) and back side (interface of coating/glass) of the copolymer were investigated using SEM/EDS.

SEM/EDS analysis<sup>17</sup> was performed on a scanning electron microscope (model JSM-840A; Japan Electron Optics Co., Tokyo, Japan) equipped with a Kevex light element detector. The X-ray detector was operated in the thin-window mode at less than 20% dead time. A Denton Desk II sputter coater, with a carbon target, was employed for coating SEM samples to reduce surface charging effect.

## RESULTS AND DISCUSSION

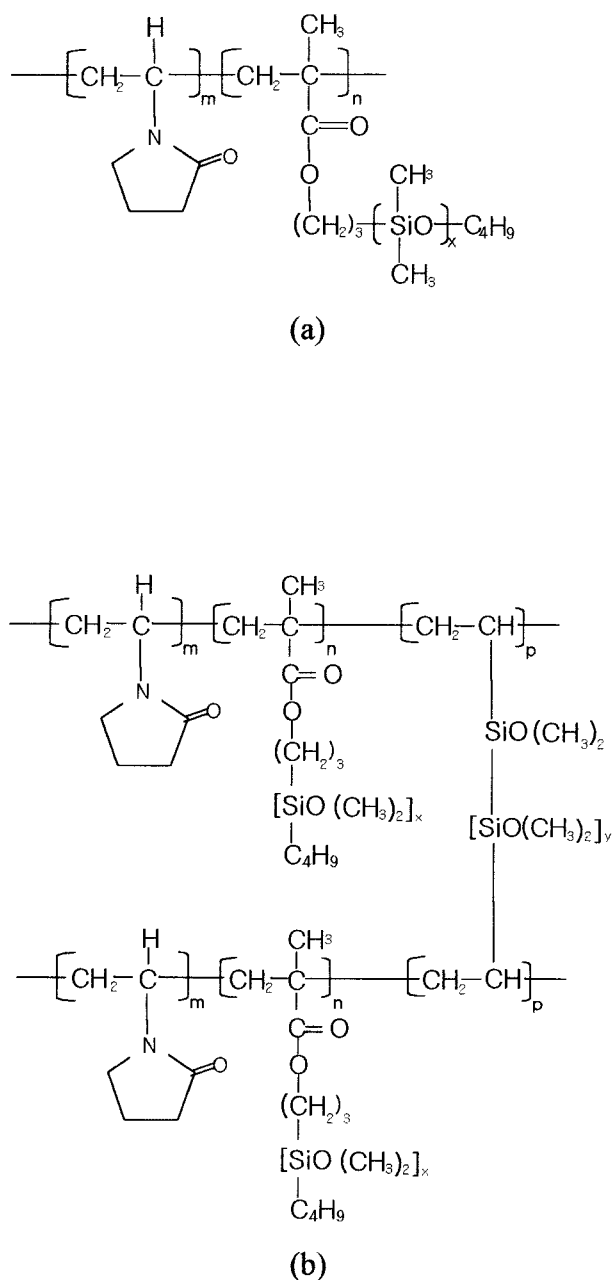
### Analysis of VP/VS Copolymers

The molecular structure of VP/VS copolymers is shown in **Scheme 1**. Figure 1(a) and (b) show the FTIR spectra of polyvinyl pyrrolidone and VP/VS copolymer, respectively. Compared with Figure 1(a), Figure 1(b) presents new Si absorption peaks, that is, Si—O—Si stretching absorption at 1085 and 1049  $\text{cm}^{-1}$ , Si—CH<sub>3</sub> rocking normal at 1287  $\text{cm}^{-1}$ , and Si—C bending absorption at 803  $\text{cm}^{-1}$ . Figure 2(a) and (b) present the <sup>13</sup>C-NMR spectra of copolymers obtained from Exp3-1 containing no crosslinking agent and from Exp3-2 containing a crosslinking agent (SV), respectively. They confirm the structure of VP/VS copolymers by the following chemical shifts: CH<sub>3</sub>—Si in VS and SV units at 0.65 ppm and C=O in VP at 175 ppm. Following the peak area ratio of 175 ppm (C=O in VP unit) to 0.65 ppm (CH<sub>3</sub>—Si in VS and SV units), it can be calculated that the weight ratio of VP unit to VS unit in copolymer from Exp3-1 is 4.5 : 1 and that of VP unit to VS and SV units in copolymer from Exp3-2 is 5 : 1. The ratios of VP unit to silicone-containing units in the copolymers were quite different from the ratios in the feeding monomers (9 : 1). It means that all the VP monomers did not readily react with silicone-containing monomers. Unfortunately, we could not distinguish CH<sub>3</sub>—Si of the SV unit from that of the VS unit in the spectrum of copolymers obtained from Exp3-2 [panel (b) in Fig. 2] because of the similarity in the chemical structure.

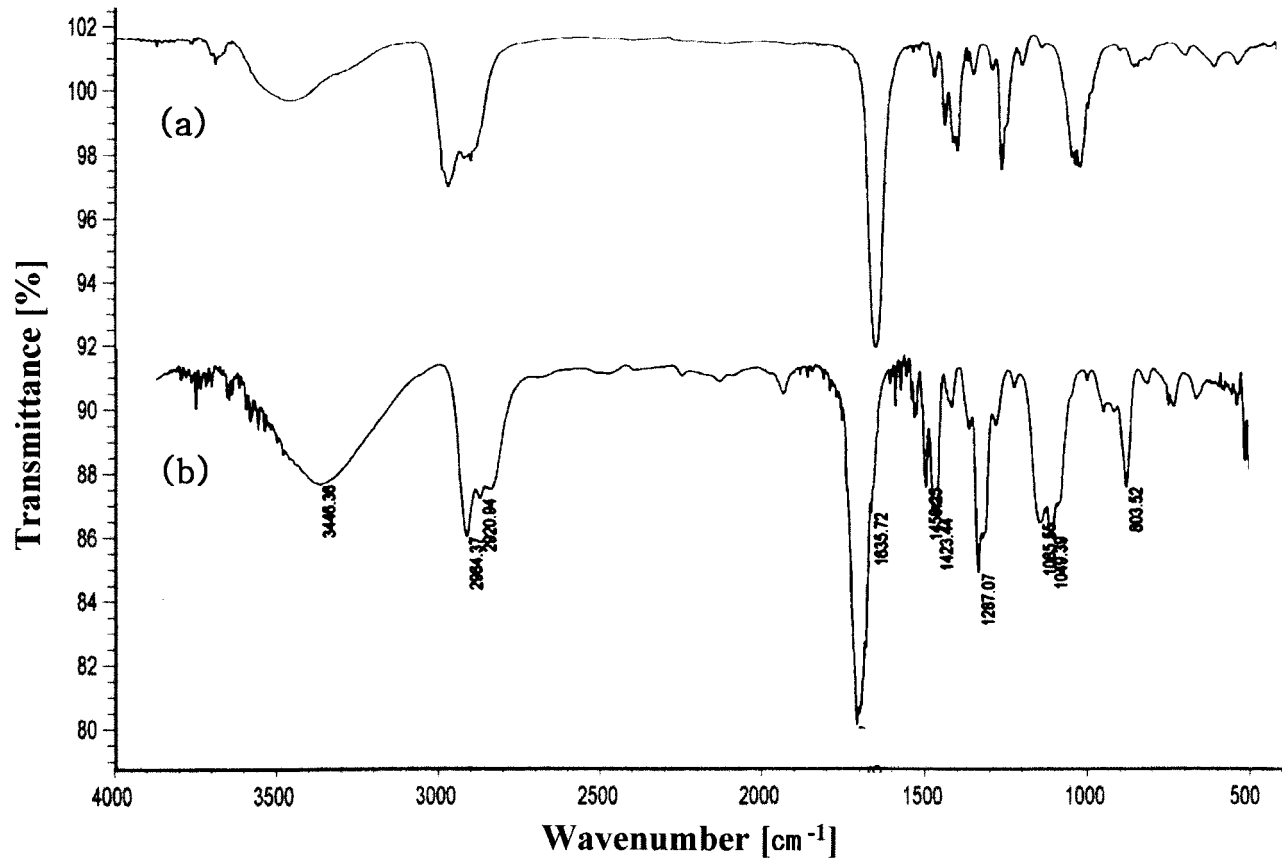
Figure 3(a) and (b) are the pyrolysis GC-Mass spectra of Exp3-1 and Exp3-2, and also certify the structure of VP/VS copolymers by the following

peak: *N*-vinyl pyrrolidone at 15.99-min retention time (RT), hexamethylcyclotrisiloxane at 9.47-min RT (Exp3-1) and *N*-vinyl pyrrolidone at 15.99-min RT, hexamethylcyclotrisiloxane at 9.47-min RT, and octamethyl cyclotetrasiloxane at 14.63-min RT (Exp3-2) by library searching.

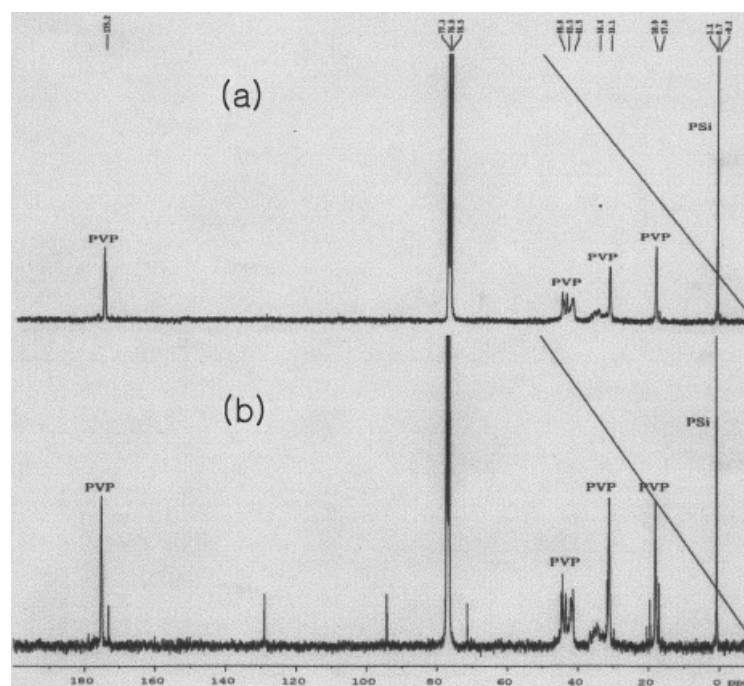
The molecular weight and distribution of VP/VS copolymer (Exp3-1, Exp3-2) were determined from the GPC elution curve [Fig. 4(a) and (b)]. The calculated average molecular weight of



**Scheme 1** The chemical structures of (a) branched VS/VP copolymers and (b) crosslinked VP/VS copolymers.



**Figure 1** FTIR spectra of (a) polyvinyl pyrrolidone and (b) VP/VS copolymers.



**Figure 2**  $^{13}\text{C}$ -NMR spectra of (a) Exp3-1 and (b) Exp 3-2.

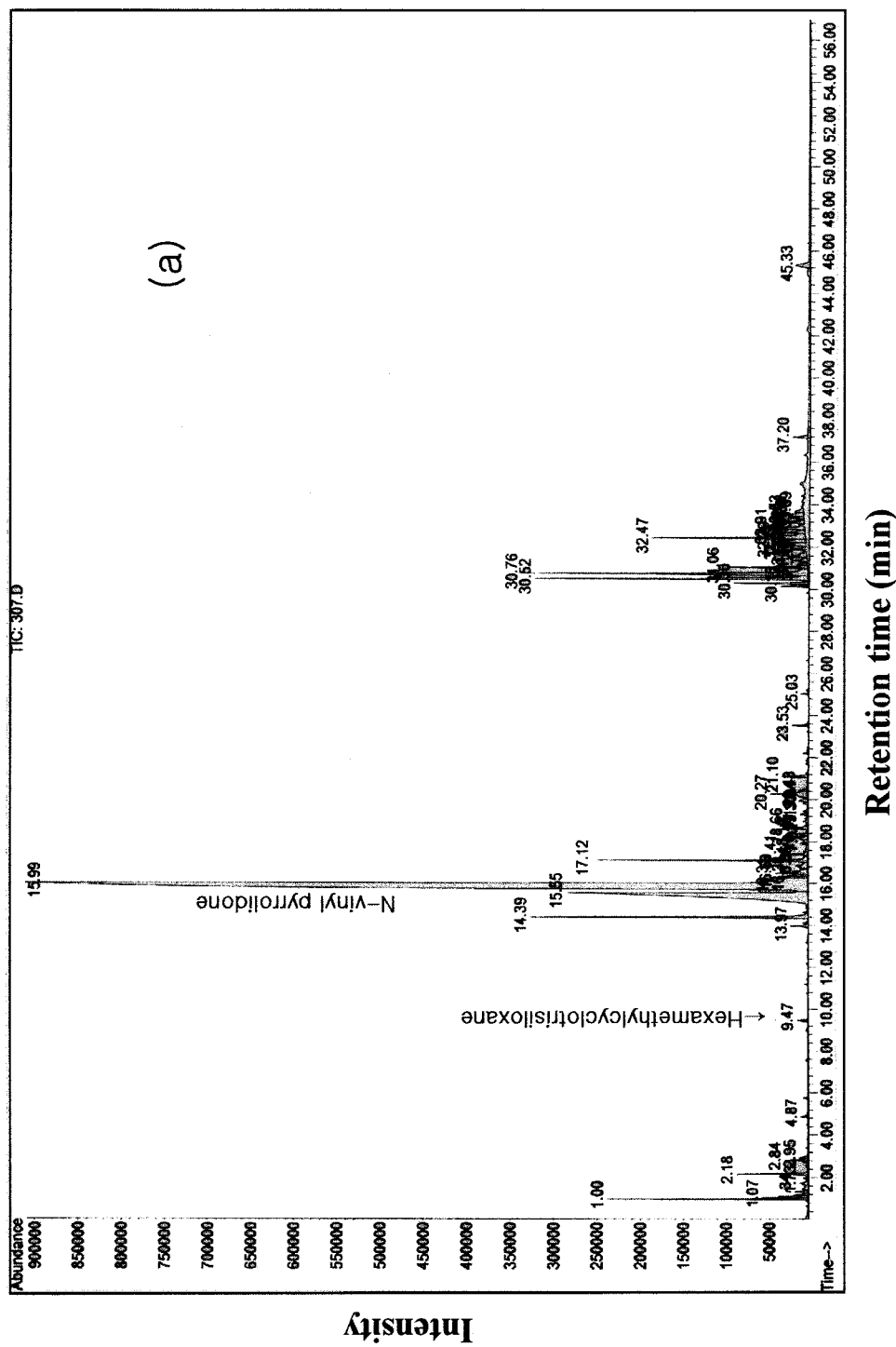
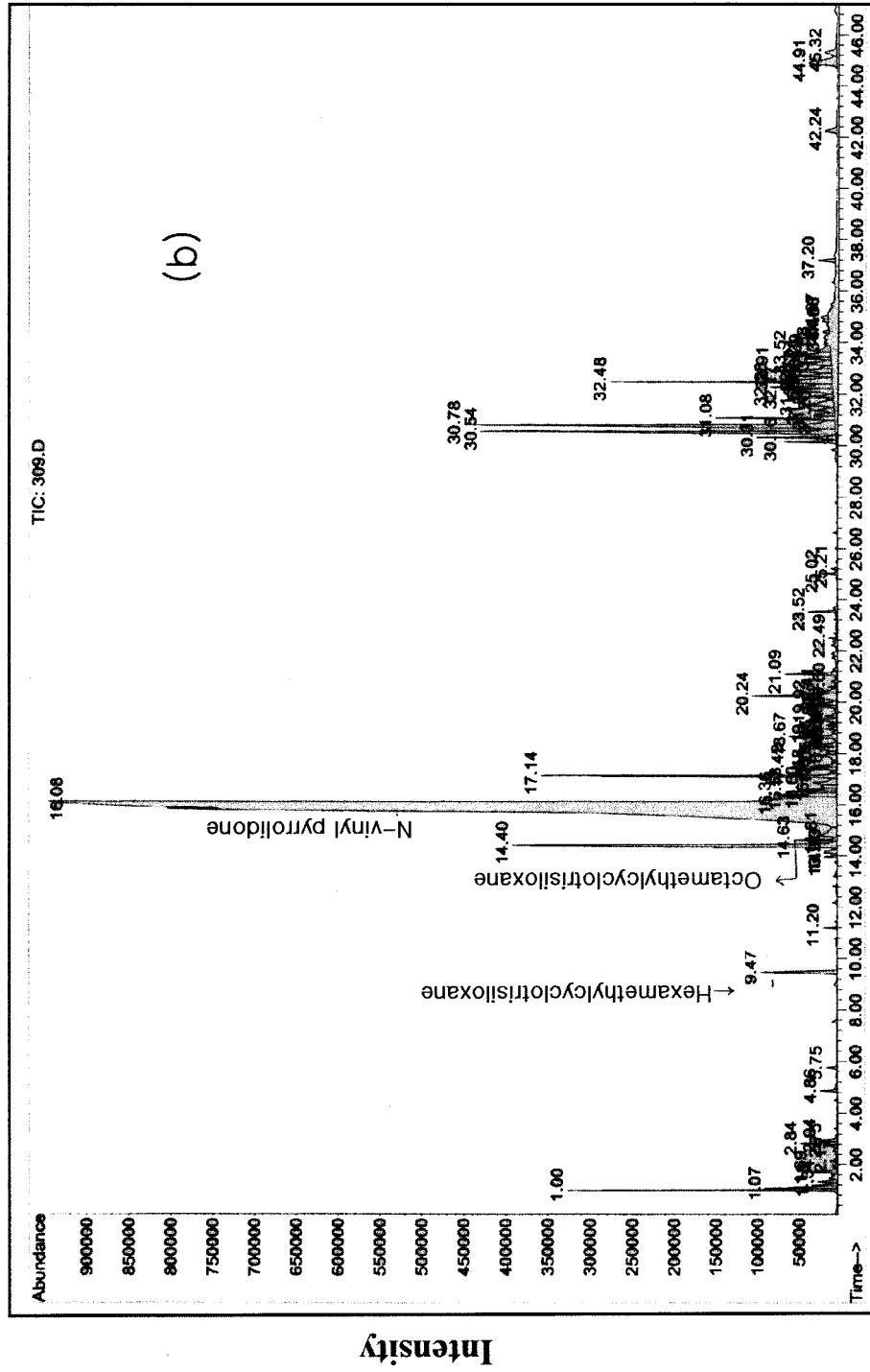
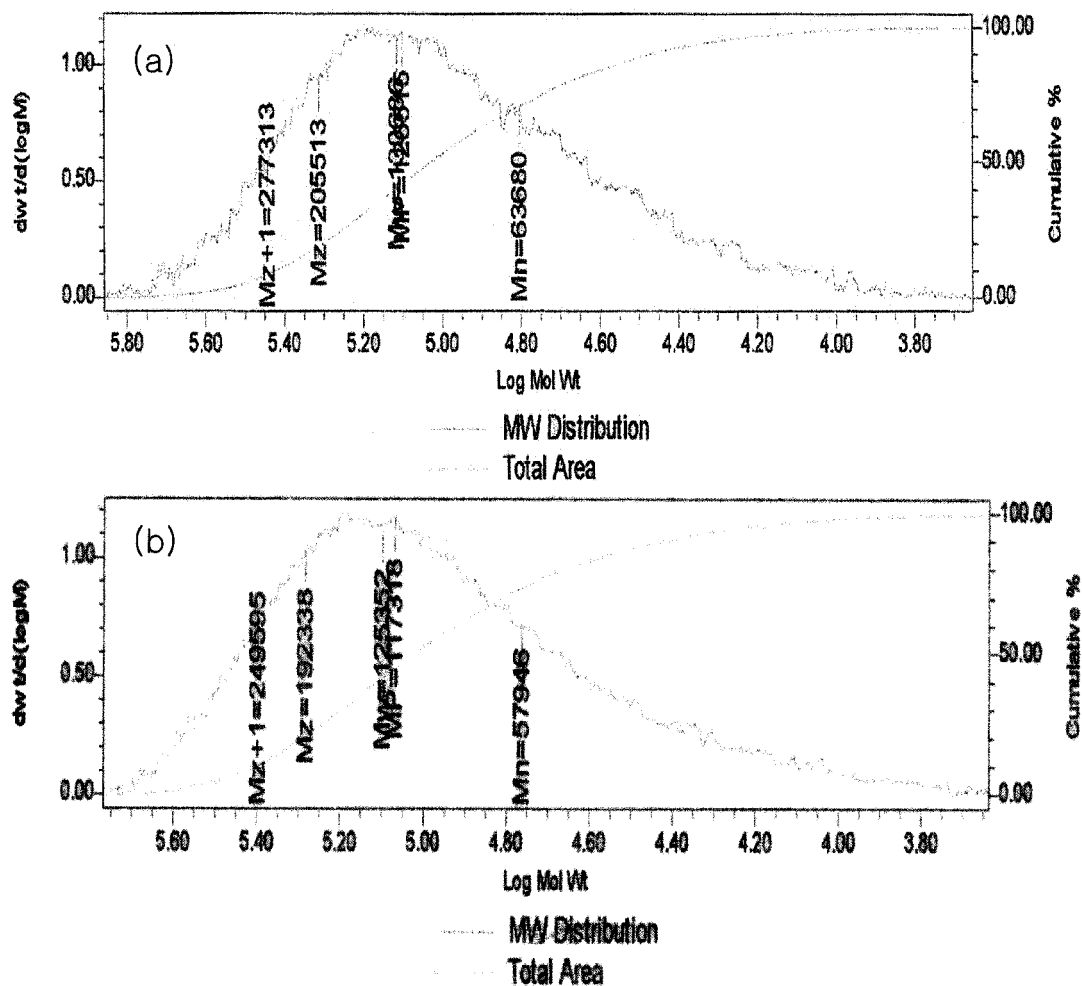


Figure 3 The spectra of pyrolysis GC-Mass of copolymers: (a) branched VPNS copolymer (Exp3-1); (b) crosslinked VPNS copolymer (Exp3-2).



Retention time (min)

Figure 3 (Continued from the previous page)



**Figure 4** GPC curves for VS/VP copolymers: (a) branched VP/VS copolymer (Exp3-1); (b) crosslinked VP/VS copolymer (Exp3-2).

Exp3-1 was  $M_n = 63,680$ ,  $M_w = 130,686$ , and polydispersity = 2.05; and that of Exp3-2 was  $M_n = 57,946$ ,  $M_w = 125,352$ , and polydispersity = 2.16, which is indicative of a fairly narrow distribution.

#### The Turbidity of VP/VS Copolymers in EtOH

Table II shows the turbidity of VP/VS copolymers in EtOH. Regardless of the molecular weight of silicone (Exp1-1, Exp2-1, and Exp3-1), the branched copolymers were readily soluble in EtOH and all the samples were transparent. However, in the case of copolymers including crosslinking agent (SV), such as Exp3-2, Exp3-3, and Exp3-4, the copolymers were not soluble in EtOH, and they exhibited significant values of turbidity. It is thought that the high turbidity results from the insoluble property of the crosslinked copolymers.

#### Thermal Analysis

Thermal transitions of VP/VS copolymers were investigated using DSC. The changes in  $T_g$ 's as functions of various molecular weights of silicone and degrees of the addition of crosslinking agent are shown in Figures 5 and 6, respectively. The lower the molecular weight and the more the crosslinking agent added, the higher the  $T_g$ 's of copolymers.

As the crosslinking density increases, the chain mobility and the number of possible conformations (entropy) decrease.<sup>19</sup> Therefore, the  $T_g$ 's of the resulting copolymers would increase.

Using the Fox equation,<sup>18</sup> the  $T_g$  value of VP/VS copolymers can be estimated as

$$\frac{1}{T_g} = \frac{w_1}{T_{g1}} + \frac{w_2}{T_{g2}}$$

**Table II** Turbidity of VP/VS Copolymers in EtOH

Designation	Exp1-1	Exp2-1	Exp3-1	Exp3-2	Exp3-3	Exp3-4
Turbidity	1.82	9	5	67.9	68.9	—

where  $w_1$  and  $w_2$  refer to the weight ratio of each unit in the copolymer, and  $T_{g1}$  and  $T_{g2}$  are their  $T_g$  values. The  $T_g$  of silicone is  $-127^\circ\text{C}$  (146 K), that of VP is  $175^\circ\text{C}$  (448 K), and the weight ratios of VP unit to silicone-containing units in copolymers are 4.5 : 1 (Exp 3-1) and 5 : 1 (Exp 3-2). Using those values, the  $T_g$  values of the copolymers obtained from Exp3-1 and Exp3-2 were estimated to be 54 and  $61.9^\circ\text{C}$ , respectively. The calculated  $T_g$  values are quite close to the observed values by DSC: Exp 3-1 ( $49^\circ\text{C}$ ) and Exp 3-2 ( $67^\circ\text{C}$ ).

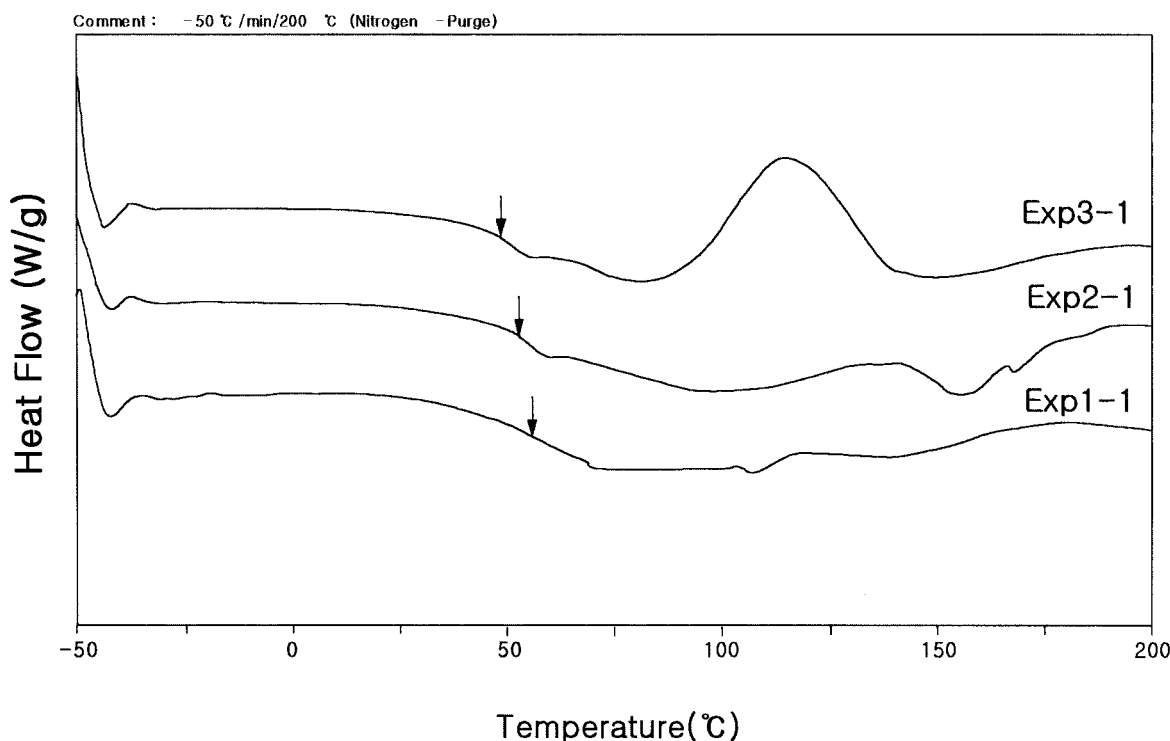
#### SEM and EDS

The surface characteristics of segregated VP/VS copolymers films cast onto a glass were investigated using SEM/EDS. Figure 7 shows the difference in surface topography of the front side (surface of the coating) and back side (interface of

coating/glass) of the copolymer film. EDS spectra for these two surfaces are shown in Figure 8. White spots of silicone were more dominant on the front side of the film than on the back side. Also, the Si peak in the EDS spectrum of the front side of film is much stronger than that of the back side (Fig. 8). Because the silicone branches (VS) of these copolymers are not significantly miscible with the hard polymer segment (VP), these polymers phase separate in dry coatings into a hard polymer segment and the silicone microdomain. The silicone phase with low surface energy would be thermodynamically forced to the front side (surface of the coating) rather than the back side (interface of coating/glass).

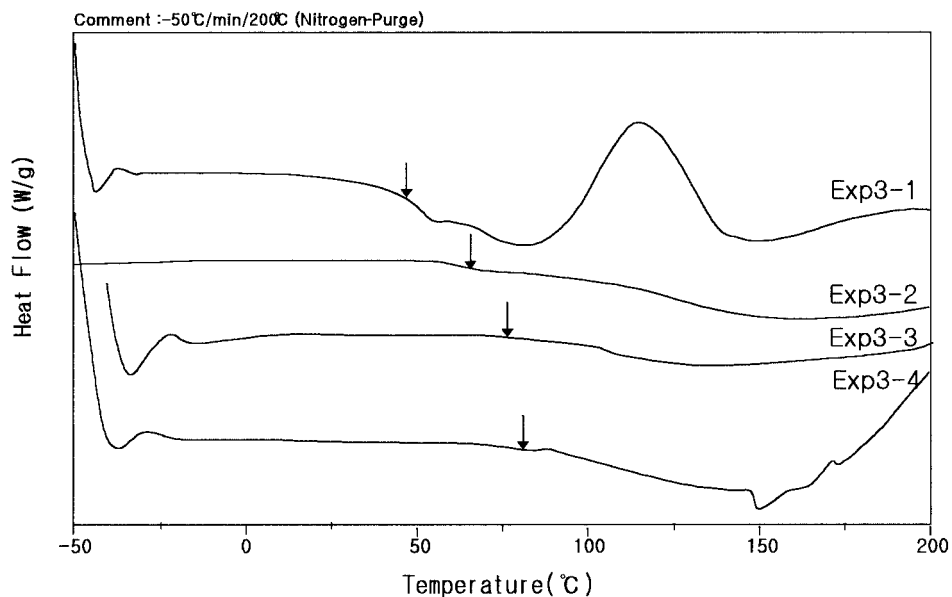
#### CONCLUSIONS

Nonionic 1-vinyl-2-pyrrolidinone/methacryloxy silicone copolymers were prepared and characterized



**Figure 5** The glass-transition temperature of VP/VS copolymers with various molecular weights of silicone.



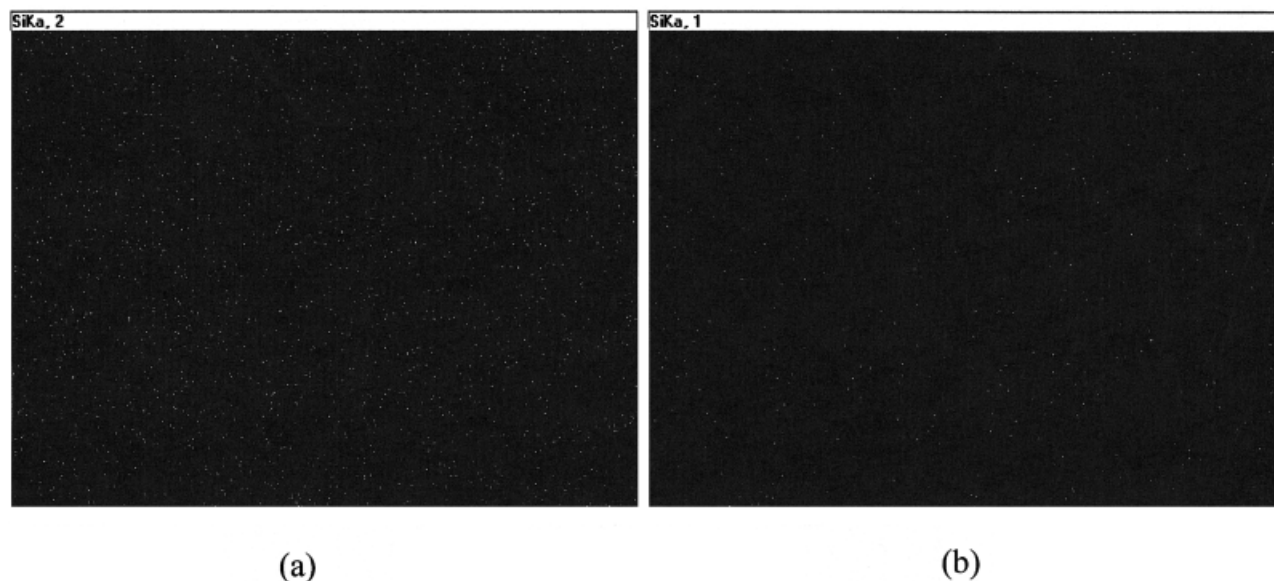


**Figure 6** The glass-transition temperature of VP/VS copolymers with various amounts of the crosslinking agent.

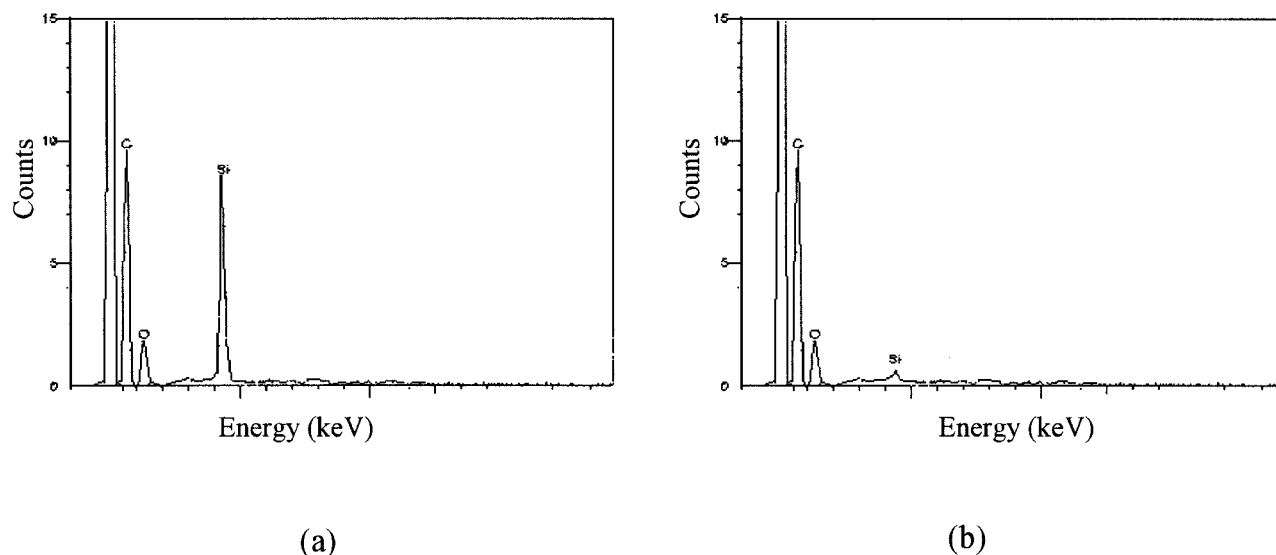
as functions of molecular weight of silicone and crosslinking density. Regardless of the molecular weight of silicone, the branched copolymers were readily soluble in EtOH. Crosslinked copolymers were not readily soluble in the solvent and they exhibited significant values of turbidity. The high turbidity would result from the insoluble property of the crosslinked polymers.

A study on the glass-transition temperatures ( $T_g$ ) of VP/VS copolymers revealed that the lower the molecular weight of silicones and the more the crosslinking agent added, the higher the  $T_g$  of the copolymers.

According to SEM/EDS study, silicone was found on the coating surface more than on the interface of coating/glass. Si-containing chains



**Figure 7** SEM micrographs of VP/VS copolymer film (at magnification  $\times 1000$ ): (a) the front side; (b) the back side.



**Figure 8** EDS spectra of VP/VS copolymer film: (a) the front side; (b) the back side.

having lower surface energy are likely to be at the coating surface more predominantly than at the interface of coating/glass. Therefore, when the copolymer is coated onto hair, Si-containing chains in the coating surface would face toward the coating/air interface, leading to a flexible sensory feeling, while giving hair a setting property because of polyvinyl pyrrolidone at the coating/hair interface.

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