

## FT-Raman Studies on Ionic Interactions in $\pi$ -Complexes of Poly(hexamethylenevinylene) with Silver Salts

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**Abstract:** Remarkably high and stable separation performance for olefin/paraffin mixtures was previously reported by facilitated olefin transport through  $\pi$ -complex membranes consisting of silver ions dissolved in poly(hexamethylenevinylene) (PHMV). In this study, the  $\pi$ -complex formation of  $\text{AgBF}_4$ ,  $\text{AgClO}_4$  and  $\text{AgCF}_3\text{SO}_3$  with PHMV and their ionic interactions were investigated. FT-Raman spectroscopy showed that the C=C stretching bands of PHMV shifted to a lower frequency upon incorporation of silver salt, but the degree of peak shift depended on the counteranions of salt due to different complexation strengths. The symmetric stretching modes of anions indicated the presence of only free ions up to  $[\text{C}=\text{C}]:[\text{Ag}]=1:1$ , demonstrating the unusually high solubility of silver salt in PHMV. Above the solubility limit, the ion pairs and higher-order ionic aggregates started to form. The coordination number of silver ion for C=C of PHMV was in the order  $\text{AgBF}_4 > \text{AgClO}_4 > \text{AgCF}_3\text{SO}_3$ , but became similar at  $[\text{C}=\text{C}]:[\text{Ag}]=1:1$ . The different coordination number was interpreted in terms of the different transient crosslinks of silver cations in the complex, which may be related to both the interaction strength of the polymer/silver ion and the bulkiness of the counteranion.

**Keywords:**  $\pi$ -complex, silver ion, poly(hexamethylenevinylene), ionic interaction, spectroscopy.

### Introduction

Polymer-metal complexes have constructed an attractive field in material science by largely improving the capacity of structural macromolecular material. The complexes have been investigated during last two decades for use as electrochemical devices such as solid state batteries, fuel cells and chemical sensors.<sup>1-3</sup> Extensive research has resulted in the understanding of ion conduction and the development of polymer electrolytes consisting of poly(ethylene oxide), poly(propylene oxide), polysiloxanes and polyphosphazenes complexed with alkali metal salts.<sup>4-7</sup> Polymer electrolytes containing silver ions are of special interest due to their possible applications to facilitated olefin transport membranes for the separation of olefin/paraffin mixtures.<sup>8-17</sup>

Physico-chemical properties and molecular structures of polymer electrolytes strongly depend on the dissociation and association behavior of metal salts in polymer solvents. Such behavior is possible because of the coordinative interaction between metal ion and electron donor group of polymer solvent<sup>1-7</sup> and thus the interaction intensity determines ion mobility and gas transport properties. Most investigations on the dissolution and complexation behavior have been performed for polymer electrolytes formed by coordination bond between metal ion and electron donor group of polymer solvent.<sup>1-7</sup> For example, the oxygen atoms in ether, amide, ester and ketone have been mostly employed as a ligand atom for coordination of metal ion such as lithium and silver ions. Previously we have reported on the complexes of silver salts with C=C in poly(hexamethylene vinylene) (PHMV) through  $\pi$ -complexation to the first and their successful application to facilitated olefin transport membranes for olefin/paraffin separation.<sup>18</sup> The PHMV/ $\text{AgBF}_4$  membrane showed high separation performance, i.e., the mixed gas

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selectivity of propylene/propane was 17 and the total permeance reached 10 GPU (1 GPU =  $1.0 \times 10^{-6}$  cm<sup>3</sup>(STP)/cm<sup>2</sup> sec cmHg), and furthermore the separation performance was remarkably stable for a long time up to 6 days. The complex membranes of silver ion with the oxygen atoms of amide groups commonly showed a poor long-term stability.<sup>19,20</sup>

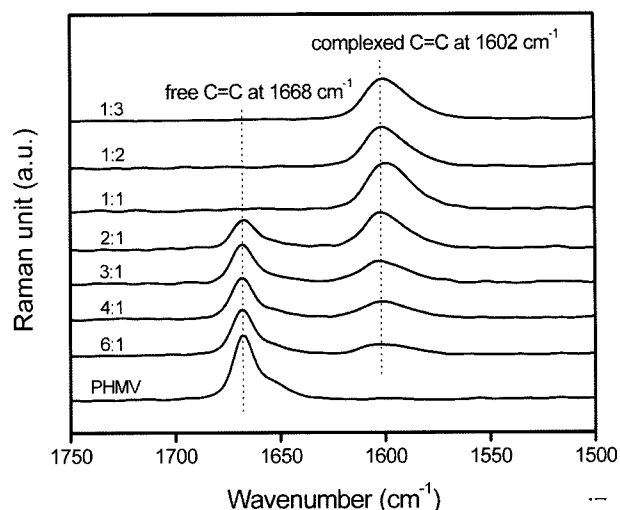
In this paper, the coordinative interaction of silver ions with C=C of PHMV and their ionic interactions with counteranions are elaborated in detail. More specifically, the dissociation and  $\pi$ -complexation behavior in PHMV complexes with three silver salts, i.e., AgBF<sub>4</sub>, AgClO<sub>4</sub> and AgCF<sub>3</sub>SO<sub>3</sub> are investigated, and ionic constituents such as free ions, ion pairs and higher order ionic aggregates are additionally characterized. A particular attention is focused on the coordination number of silver ions for C=C of PHMV to provide insight into the molecular structure and complexation formation of  $\pi$ -complex polymer electrolytes.

## Experimental

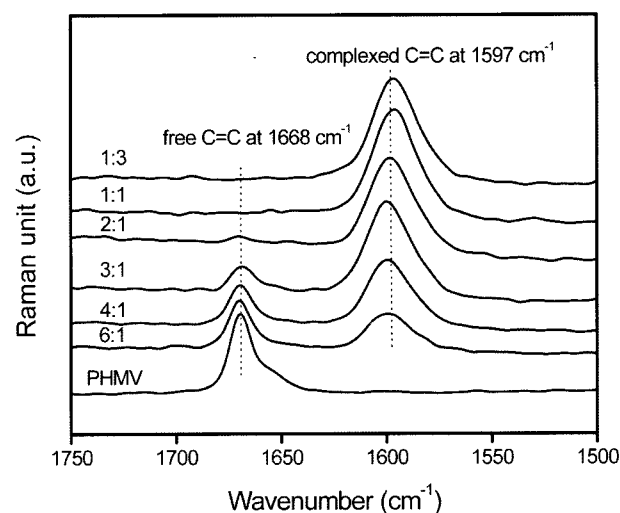
Poly(hexamethylenevinylene) (PHMV,  $M_w$  = 100,000 g/mol), silver tetrafluoroborate (AgBF<sub>4</sub>, 98%), silver perchlorate (AgClO<sub>4</sub>, 99.9%) and silver trifluoromethanesulfonate (AgCF<sub>3</sub>SO<sub>3</sub>, 99 +%) were purchased from Aldrich Chemical Co. and were used without further purification. PHMV solutions were prepared by dissolving 10 wt% PHMV in tetrahydrofuran (THF, 99+%, Aldrich) with stirring at room temperature. After complete dissolution, the predetermined amounts of Ag salt were added in the solution depending on the mole ratio of [C=C]:[Ag]. The solutions were then cast on teflon-attached glass plate and dried under N<sub>2</sub> environment. The films were further dried in a vacuum oven for two days at room temperature. Raman spectra were collected for PHMV/Ag salt complexes at room temperature using Perkin Elmer System 2000 NIR FT-Raman. This experimental apparatus includes a neodymium-doped yttrium aluminum garnet (NdYAG) laser operating at 1064 nm.

## Results and Discussion

Figure 1 presents the FT-Raman spectra in the C=C stretching region for neat PHMV and PHMV/AgCF<sub>3</sub>SO<sub>3</sub> complexes with various mole ratios of [C=C]:[Ag]. The intensity of the free C=C stretching band of uncomplexed pure PHMV at 1668 cm<sup>-1</sup> decreased with increasing concentrations of silver salt and disappeared at silver concentrations above [C=C]:[Ag] = 1:1. A new band at 1602 cm<sup>-1</sup> appeared upon addition of AgCF<sub>3</sub>SO<sub>3</sub> and its intensity grew with increasing concentrations of silver salt. This new band is attributable to  $\pi$ -complexation between the silver ion and C=C bond of PHMV. The shift of the free C=C band to a lower wavenumber may originate from loosening of the C=C double bond by this coordination.<sup>14,15</sup> The uncomplexed free C=C band in PHMV/AgCF<sub>3</sub>SO<sub>3</sub> complex was evident up to



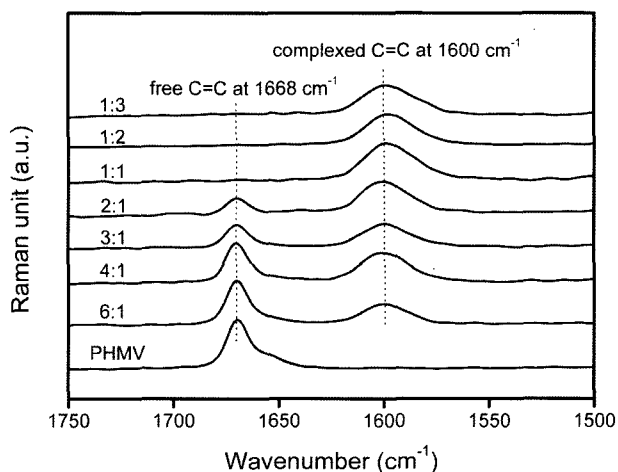
**Figure 1.** FT-Raman spectra for C=C stretching mode of pure PHMV and PHMV/AgCF<sub>3</sub>SO<sub>3</sub> complexes with various mole ratios of [C=C]:[Ag].



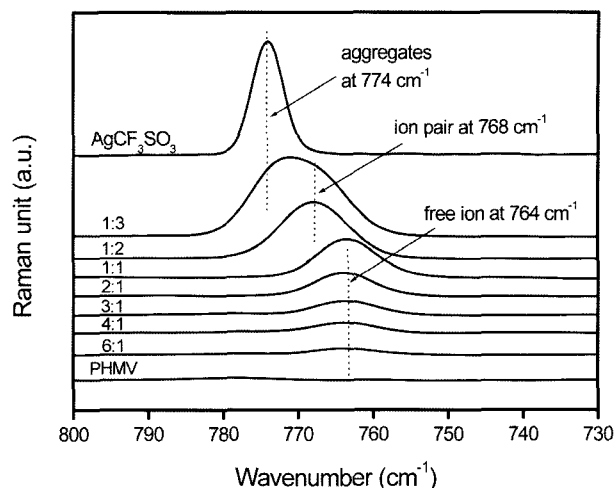
**Figure 2.** FT-Raman spectra for C=C stretching mode of pure PHMV and PHMV/AgBF<sub>4</sub> complexes with various mole ratios of [C=C]:[Ag].

[C=C]:[Ag] = 2:1, but disappeared completely at 1:1. Thus, the 1:1 PHMV/AgCF<sub>3</sub>SO<sub>3</sub> complex has only one C=C band. This strongly suggests that for a range of [C=C]:[Ag] up to a maximum mole ratio of 1:1, there exists  $\pi$ -complexation between the silver ion and C=C bond of PHMV.

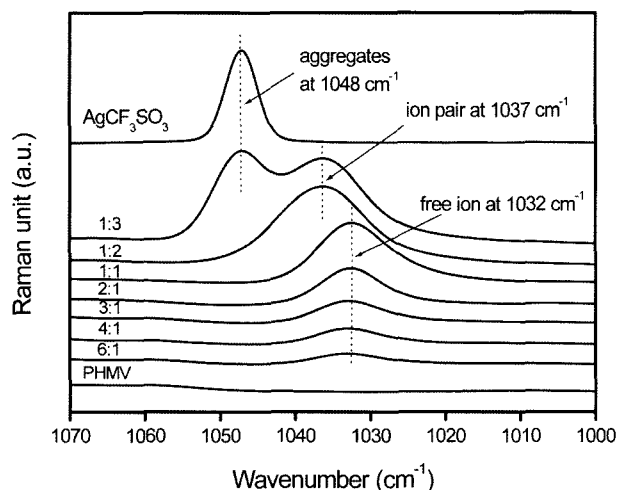
Figures 2 and 3 show the FT-Raman spectra of PHMV/AgBF<sub>4</sub> and PHMV/AgClO<sub>4</sub> complexes with various mole ratios of [C=C]:[Ag], respectively. The vibrational FT-Raman spectra of PHMV/AgBF<sub>4</sub> and PHMV/AgClO<sub>4</sub> complexes in the C=C stretching region were almost identical to those of PHMV/AgCF<sub>3</sub>SO<sub>3</sub> complexes except for small differences in the band position. Since the shift of the C=C



**Figure 3.** FT-Raman spectra for C=C stretching mode of pure PHMV and PHMV/AgClO<sub>4</sub> complexes with various mole ratios of [C=C]:[Ag].



**Figure 5.** FT-Raman spectra for CF<sub>3</sub> bending mode of AgCF<sub>3</sub>SO<sub>3</sub>, pure PHMV and PHMV/AgCF<sub>3</sub>SO<sub>3</sub> complexes with various mole ratios of [C=C]:[Ag].



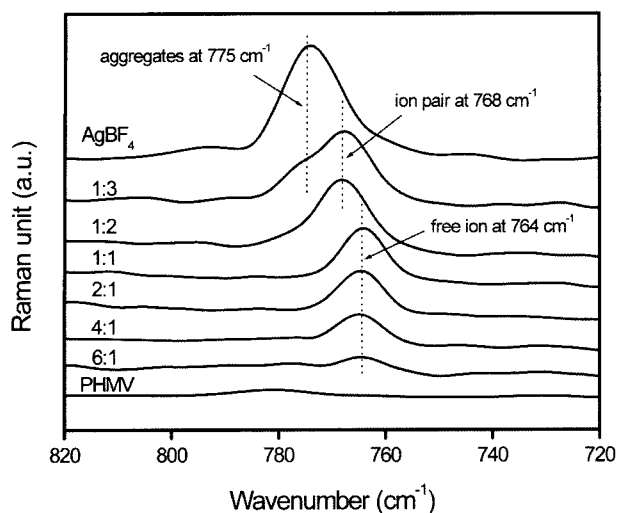
**Figure 4.** FT-Raman spectra for SO<sub>3</sub><sup>-</sup> stretching mode of AgCF<sub>3</sub>SO<sub>3</sub>, pure PHMV and PHMV/AgCF<sub>3</sub>SO<sub>3</sub> complexes with various mole ratios of [C=C]:[Ag].

band comes from the loosening of the C=C double bond, the interaction strength between silver ion and PHMV can be estimated in terms of the magnitude of this band shift.<sup>15</sup> Thus, it is expected that the complexation strength between silver ion and C=C bond of PHMV has the following order: AgBF<sub>4</sub> (1597 cm<sup>-1</sup>) > AgClO<sub>4</sub> (1600 cm<sup>-1</sup>) > AgCF<sub>3</sub>SO<sub>3</sub> (1602 cm<sup>-1</sup>).

It is known that the anion stretching mode of Raman spectra varies depending on the ionic species of free ions, ion pairs and higher ionic aggregates,<sup>21-26</sup> providing quantitative information on the dissociation and association behavior of salts. The Raman spectra of the  $\nu_s$  stretching of SO<sub>3</sub><sup>-</sup> for the triflate in PHMV/AgCF<sub>3</sub>SO<sub>3</sub> with various mole ratios of

[C=C]:[Ag] are shown in Figure 4. Up to 1:1 PHMV/AgCF<sub>3</sub>SO<sub>3</sub>, a single band at 1032 cm<sup>-1</sup> was observed which is associated with the presence of the free anion.<sup>21</sup> When the silver concentration was increased to 1:2, the main band shifted to a higher wavenumber and the band became asymmetric. The asymmetric shape of the band may be attributed to the existence of both free anions and ion pairs. When the silver concentration was further raised to 1:3 PHMV/AgCF<sub>3</sub>SO<sub>3</sub>, the bands of ion pairs at 1037 cm<sup>-1</sup> and higher-order ionic aggregates at 1048 cm<sup>-1</sup> were observed. It should be noted that the pure AgCF<sub>3</sub>SO<sub>3</sub> is composed of higher-order ionic aggregates. The ionic constituents of silver salt in PHMV/AgCF<sub>3</sub>SO<sub>3</sub> complexes can be also identified by the FT-Raman spectra for  $\delta_s$  (CF<sub>3</sub>) bending modes. As shown in Figure 5, only free ions were present at silver concentrations up to 1:1 relative to C=C, above which ion pairs started to form, followed by higher-order ionic aggregates, which is consistent with the results of  $\nu_s$  (SO<sub>3</sub><sup>-</sup>). In the case of poly(*N*-vinyl pyrrolidone) (PVP,  $M_w$  = 1,000,000 g/mol) complexes with silver salt, the behavior of ionic constituents by  $\nu_s$  (SO<sub>3</sub><sup>-</sup>) mode was different from that by  $\delta_s$  (CF<sub>3</sub>), which was attributed to a steric effect by highly entangled polymer chains.<sup>17</sup> Thus, the steric hindrance for ion coordination with PHMV seems to be negligible.

Figure 6 presents the FT-Raman spectra for  $\nu_2$  (BF<sub>4</sub><sup>-</sup>) for the neat PHMV and PHMV/AgBF<sub>4</sub> complexes as a function of mole ratio of [C=C]:[Ag]. Similar to the behavior of PHMV/AgCF<sub>3</sub>SO<sub>3</sub> complexes, only free ions were present at silver concentrations up to 1:1, ion pairs formed at 1:2 and higher-order ionic aggregates appeared at 1:3. To obtain the descriptive information, the Raman spectra for PHMV/AgCF<sub>3</sub>SO<sub>3</sub> and PHMV/AgBF<sub>4</sub> complexes at [C=C]:[Ag] = 1:1, 1:2 and 1:3 were deconvoluted as seen in Figures 7 and

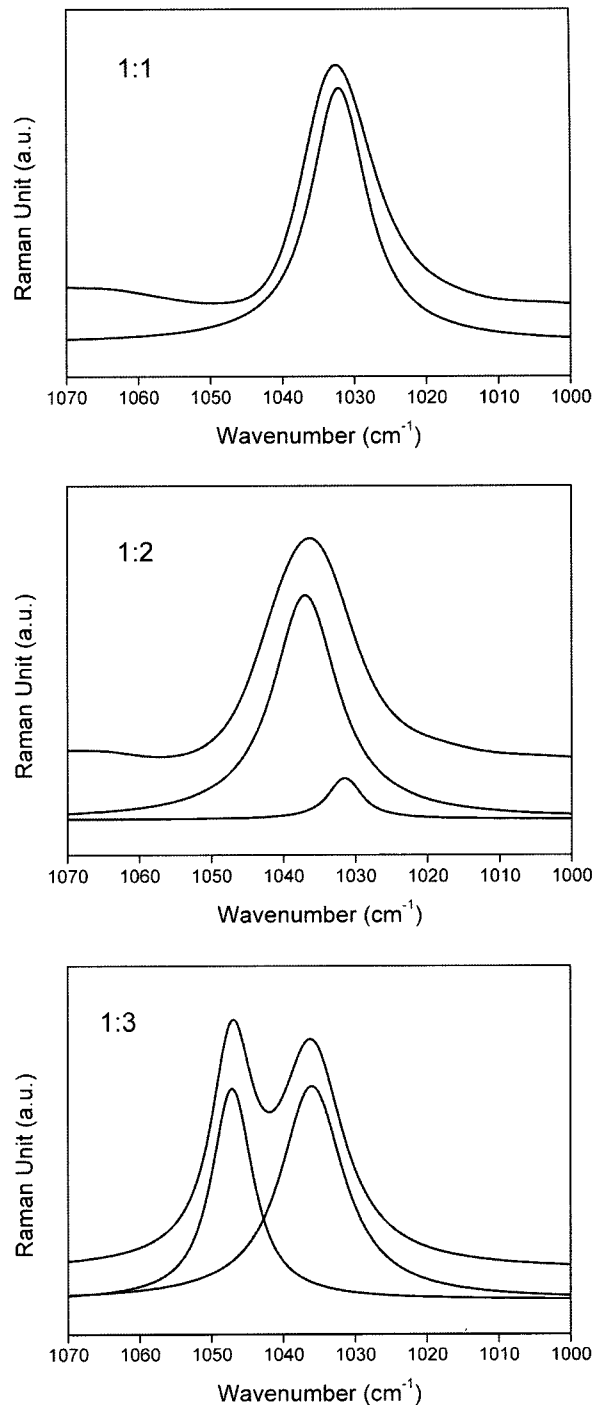


**Figure 6.** FT-Raman spectra for  $\text{BF}_4^-$  stretching mode of  $\text{AgBF}_4$ , pure PHMV and PHMV/ $\text{AgBF}_4$  complexes with various mole ratios of  $[\text{C}=\text{C}]:[\text{Ag}]$ .

8, respectively. The relative concentrations of each ionic species were calculated as the ratio of the deconvoluted area under the peak with maximum value to the total area of the band envelope<sup>27,28</sup> and summarized in Table I.

The coordination number of the silver ion for  $\text{C}=\text{C}$  of PHMV was obtained from the concentration ratio of complexed  $\text{C}=\text{C}$  to free silver ions up to  $[\text{C}=\text{C}]:[\text{Ag}]=1:1$ . The coordination numbers of silver ions for the PHMV complexes with  $\text{AgBF}_4$ ,  $\text{AgClO}_4$  and  $\text{AgCF}_3\text{SO}_3$  as a function of silver concentration are plotted in Figure 9. As seen, the coordination numbers of silver ion for  $\text{C}=\text{C}$  of PHMV monotonously decreased with increasing silver concentrations. The coordination numbers of PHMV complexes are found to be always higher than those of poly(2-ethyl-oxazoline) (POZ) complexes containing amide group at the use of the same silver salt.<sup>16</sup> This result may be due to the different complex structure each other. It is also found that the coordination number of silver ion is strongly dependent on the counteranion of salt and has the order of  $\text{AgBF}_4 > \text{AgClO}_4 > \text{AgCF}_3\text{SO}_3$ . However their values become similar at high concentration of silver salt, i.e.  $[\text{C}=\text{C}]:[\text{Ag}]=1:1$ .

Different coordination number in three kinds of salt system at low concentrations of silver salt can be interpreted in terms of the different transient crosslinks of silver cations.<sup>10</sup> Transient crosslink may be related to the strength of coordinative interaction between polymer chains and silver cations. When the coordinative interaction of polymer with silver ion is strong, transient crosslink will be stronger, and vice versa. Thus,  $\text{AgBF}_4$  complex with stronger interaction of polymer/silver ion has a higher coordination number than other systems at the same mole ratio of  $[\text{Ag}]/[\text{C}=\text{C}]$ . Another effect might come from the steric hindrance of bulky  $\text{CF}_3\text{SO}_3^-$  anions for silver-polymer complexation, leading to

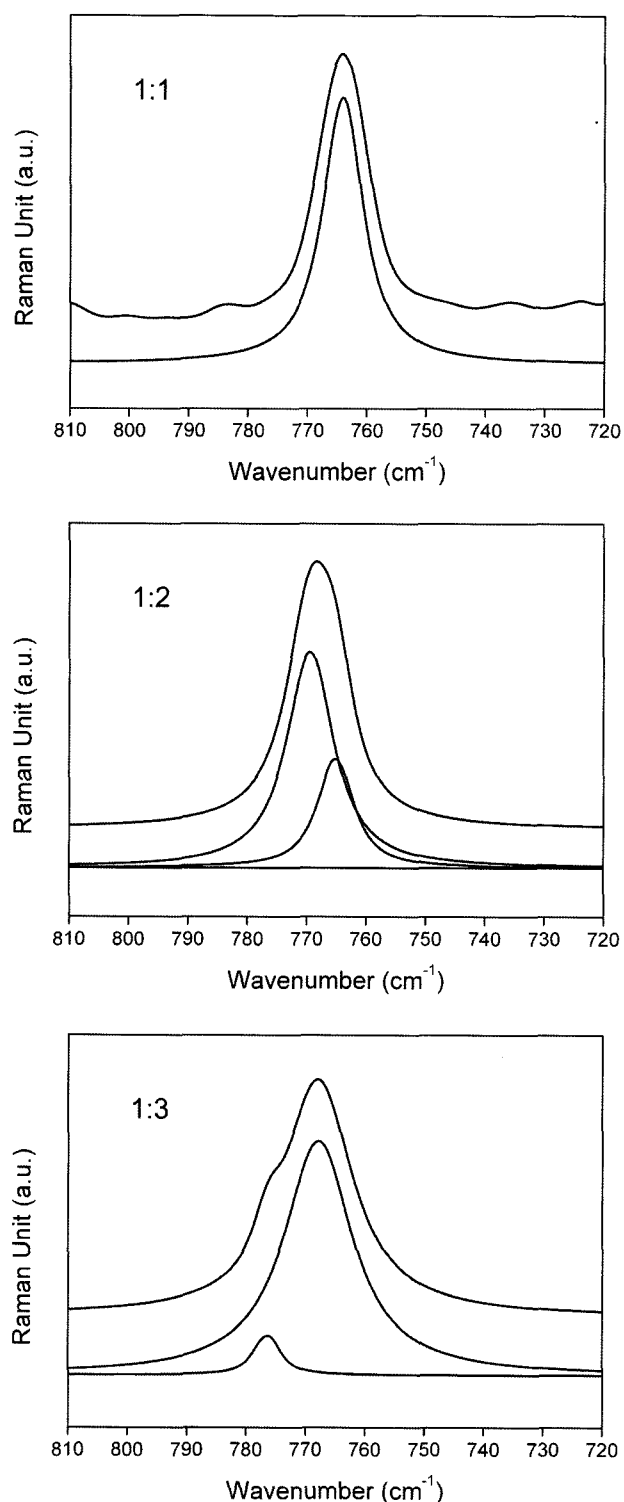


**Figure 7.** Deconvoluted curves of  $\text{SO}_3^-$  stretching mode for 1:1, 1:2 and 1:3 PHMV/ $\text{AgCF}_3\text{SO}_3$  complexes.

relatively lower coordination number of silver ions to  $\text{C}=\text{C}$  groups in  $\text{AgCF}_3\text{SO}_3$  complex.

## Conclusions

Silver salts of  $\text{AgBF}_4$ ,  $\text{AgClO}_4$  and  $\text{AgCF}_3\text{SO}_3$  were dis-

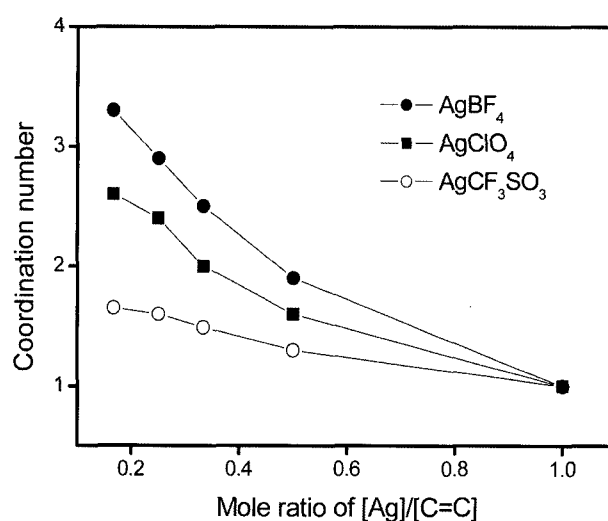


**Figure 8.** Deconvoluted curves of  $\text{BF}_4^-$  stretching mode for 1:1, 1:2 and 1:3 PHMV/ $\text{AgBF}_4$  complexes.

solved in polymer matrix of PHMV due to the  $\pi$ -complexation of silver ions and C=C group. The ionic constituents of the salts in PHMV  $\pi$ -complexes of silver salt were char-

**Table I.** The Relative Concentrations of Ionic Species in PHMV/Silver Salt Complexes

Salt	[C=C]:[Ag]	Free Ions	Ion Pairs	Aggregates
$\text{AgBF}_4$	< 1:1	100.0%	0.0%	0.0%
	1:2	27.7%	72.3%	0.0%
	1:3	0.0%	94.1%	5.9%
$\text{AgClO}_4$	< 1:1	100.0%	0.0%	0.0%
	1:2	15.5%	84.5%	0.0%
	1:3	0.0%	82.0%	18.0%
$\text{AgCF}_3\text{SO}_3$	< 1:1	100.0%	0.0%	0.0%
	1:2	8.5%	91.5%	0.0%
	1:3	0.0%	61.0%	39.0%



**Figure 9.** Coordination number of silver ion for C=C in PHMV/silver salt complexes.

acterized by anion vibration mode of FT-Raman spectroscopy. At silver concentrations above  $[\text{C}=\text{C}]:[\text{Ag}]=1:1$ , ion pairs started to form, followed by higher order ionic aggregates. The coordination number of silver ion for C=C of PHMV decreased with silver concentration and exhibited the order of  $\text{AgBF}_4 > \text{AgClO}_4 > \text{AgCF}_3\text{SO}_3$ , but approached to be similar as unity. Different coordination number was attributed to the different transient crosslinks of silver cations in the complex, which is related to both the interaction strength of polymer/silver ion and the bulkiness of counter-anion.

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