

# Studies on Self-Assembly and Characterization of Polyelectrolytes and Organic Dyes

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**ABSTRACT:** Four polyelectrolyte complexes were formed through self-assembly of poly-*N*-ethyl-*N,N*-(dimethylamino)-ethyl methacrylate (PEDEM) and poly-*N*-ethyl-4-vinylpyridinium (PEVP) cations with methyl orange (MO) and metanil yellow (MY) anions in water. The FTIR spectra showed that the assembly was formed chiefly through electrostatic force and hydrophobic interaction between polyelectrolytes and organic dyes without new bonds emerging. The fluorescence spectra revealed that the emission waves of the complexes of PEDEM–MY and PEDEM–MO in alcohol were

blue-shifted in comparison with that of dyes in alcohol, and the emission waves of the PEVP–MY and PEVP–MO complexes in alcohol were red-shifted in comparison with that of dyes in alcohol. The structure of the complexes in the solid state were also investigated by DTA and X-ray diffraction experiments. It could be proved that the complexes were new materials formed through weak interactions. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 87: 369–374, 2003

**Key words:** self-assembly; polyelectrolytes; dyes

## INTRODUCTION

Nowadays, supramolecular chemistry is an important field in the development of chemistry since the French scientist J. M. Lehn first expounded the conception in a speech when he won the Nobel prize.<sup>1,2</sup> In polymer science, polyelectrolytes are always chosen as the model in studies on supramolecular assembly for the following reasons.<sup>3</sup> First, polyelectrolytes have special molecular frameworks and high sensitivity to exterior condition changes. Second, they have many frame forms in nanometer microcosmic scale and can vary with the change of the parameter of the microcosmic circumstance. Third, almost all important biologic macromolecules such as polypeptides, polysaccharides, and DNA are polyelectrolytes. Studies on the supramolecular assembly of polyelectrolytes can also provide some help in explaining special life-function courses.<sup>4,5</sup> Different complexes can be formed through different polyelectrolyte assemblies with different surfactants or dyes. The complexes can be used in dyeing, liquid crystal displays (LCD), nonlinear optics, food, medicine, chromatograms, and some other new technical fields.<sup>6,7</sup> (It is difficult to acquire polycations, therefore, studies on supramolecular assemblies of polycations are relatively few compared to those on supramolecular assemblies of polyanions.) Polycations

such as poly(*N*-alkyl vinylpyridine), lonene-*n,n*, polyviologen, polyaniline, and polypyrrole have been reported in the literature.<sup>8</sup>

In present article, the bromine salt form of poly-*N*-ethyl-*N,N*-(dimethylamino)ethyl methacrylate (PEDEM–Br) was first used for a polyelectrolyte cation template to assemble with dyes, and poly-*N*-ethyl-4-vinylpyridinium bromine salt (PEVP–Br) was also used to assemble with dyes. Studies on FTIR spectra showed that the assembly was processed mainly through electrostatic force and hydrophobic interaction. The fluorescence spectra revealed that the emission waves of the complexes differed from those of dyes in alcohol. Furthermore, DTA and X-ray diffraction techniques were used to investigate the structures of the complexes.

## EXPERIMENTAL

### Materials

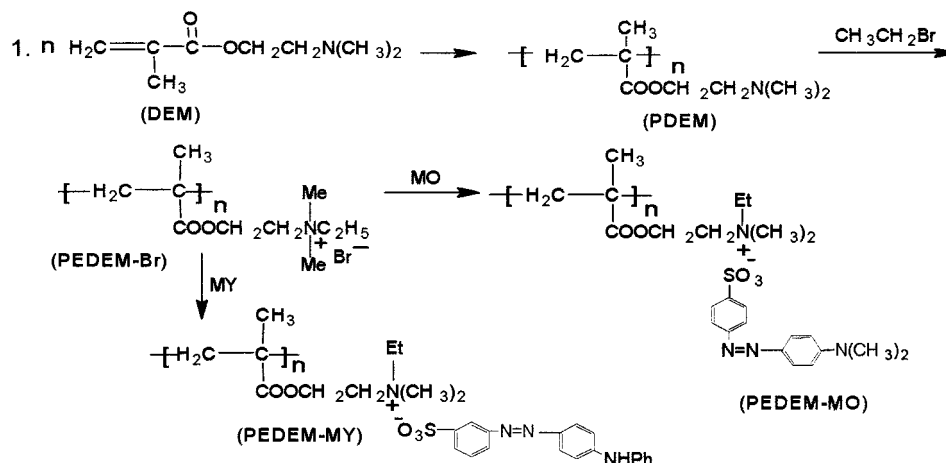
The monomers used in the preparation of polyelectrolytes included *N,N*-(dimethylamino)ethyl methacrylate (DEM) and 4-vinylpyridine (VP; chemically pure). The dyes were methyl orange (MO) and metanil yellow (MY). The solvents included NaOH, THF, ethyl acetate, bromoethane, nitrobenzene, ammonium peroxydisulfate, and sodium hydrogen sulfite (NaHSO<sub>3</sub>). The above dyes and solvents were analytically pure (Beijing Chemical Co., Beijing China).

### Measurements

A Nicolet 1700SX FTIR (all samples grounded in KBr), a Hitachi 850 fluorescence apparatus (less than 1 wt %

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Scheme 1

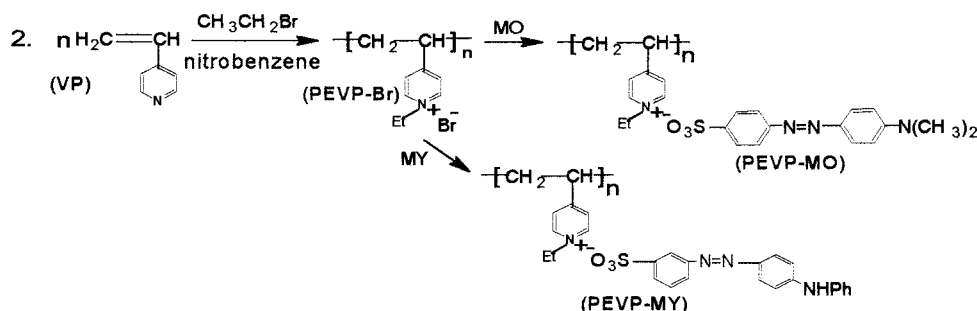
concentration in alcohol), a Shanghai CDR-1 differential thermal analysis (DTA) apparatus (samples were in the nature of powder and protected by nitrogen, whose velocity of flow was 40 mL/min, and the scanning speed was 10°C/min), and a D/max-ra X-ray diffraction apparatus were employed.

### Sample preparation

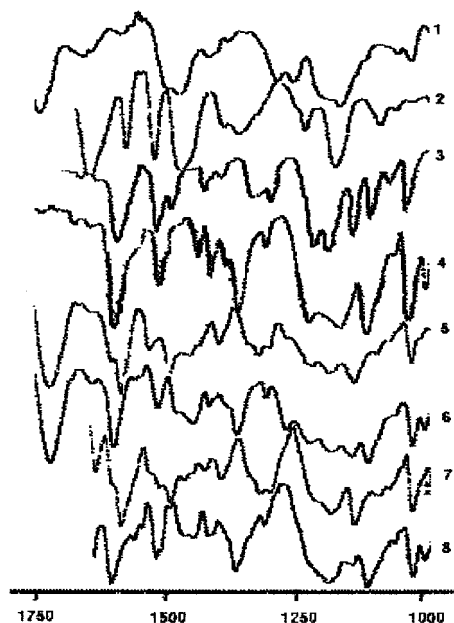
1. In a three-necked reaction vessel (250 mL), DEM (20 mL), which must be purified through distillation before use,  $(\text{NH}_4)_2\text{S}_2\text{O}_8$  (0.84 g),  $\text{NaHSO}_3$  (1.68 g), and  $\text{H}_2\text{O}$  (100 mL) were added, then heated to 70–90°C for 7 h with agitation under the protection of  $\text{N}_2$ . After that, a white suspension could be observed. Then, the solution was cooled to room temperature until it became transparent. Next, an NaOH aqueous solution (25% w/w) was added drop by drop until the white precipitation no longer increased. The precipitation was washed several times by high pure water and put in a vacuum for 48 h. The product was poly-*N,N*-(dimethylamino)ethyl methacrylate (PDEM).
2. Excessive bromoethane was added to a 5 wt % solution of PDEM in THF, then agitated at 40°C for 12 h under the protection of  $\text{N}_2$ . The final product was recovered by complete removal of

the solvent and the excessive alkyl halide and put in a vacuum for 2 days. The product was PEDEM-Br, whose inherent viscosity was 590.5 (mL/g) in water determined by a Ubbelohde viscometer at the temperature  $25 \pm 0.1^\circ\text{C}$ .<sup>9</sup>

3. VP was purified through reducing pressure distillation before use. A 5.72 mol/L solution of VP was prepared in nitrobenzene; the same concentration of a solution of bromoethane was also prepared in nitrobenzene. The same volume of the two solutions was added into an ampule vessel; then, it was sealed after the air in it was expelled by  $\text{N}_2$ . After that, the ampule vessel was put in hot water at 50–60°C for 3 days. The product was washed and precipitated by ethyl acetate. The precipitation was dried in a vacuum for 48 h; the final product was PEVP-Br,<sup>10</sup> whose inherent viscosity was 142.2 (mL/g) in water at the temperature  $25 \pm 0.1^\circ\text{C}$ .<sup>10</sup>
4. The same concentration (<1 wt %) of aqueous solutions of PEDEM-Br, PEVP-Br, MY, and IMO were prepared first. Then, the PEDEM-Br solution was added to the MY solution drop by drop with agitation until the red precipitation no longer increased. The precipitation was washed several times with highly purified water and dried in a vacuum for 48 h. The final product was a PEDEM-MY complex. In the same conditions, the complexes of PEDEM-MO, PEVP-MY, and PEVP-MO were prepared. The stoichiometry of



Scheme 2



**Figure 1** IR spectra of samples: (1) PEDEM-Br; (2) PEVP-Br; (3) MY; (4) MO; (5) PEDEM-MY; (6) PEDEM-MO; (7) PEVP-MY; (8) PEVP-MO.

these complexes was approximately 1:0.8 (polyelectrolyte to small molecule).

- The method of molarity was employed to determine the degree of quaternization of PEDEM-Br and PEVP-Br. Three kinds of aqueous solutions in certain concentrations, including  $\text{AgNO}_3$ , PEDEM-Br, and PEVP-Br, were prepared. Then, the  $\text{AgNO}_3$  solution was added into the PEDEM-Br solution drop by drop with the  $\text{K}_2\text{CrO}_4$  solution as an indicator. It was the endpoint when the color of the PEDEM-Br solution turned from yellow to red. The quaternary degree of PEDEM-Br was 72.5% and that of PEVP-Br was 94.1%. The difference was probably caused by the space effect.

## RESULTS AND DISCUSSION

### Syntheses

The syntheses routes of PEDEM-Br and the complexes PEDEM-MY and PEDEM-MO are shown in Scheme

**TABLE I**  
Attribution of the IR Vibration Peaks

Wavenumber ( $\text{cm}^{-1}$ )	Vibration mode
1729	$\nu(\text{C}=\text{O})$ (PEDEM-Br)
1655	$\nu(\text{NR}_4)$ (PEDEM-Br)
1644	$\nu(\text{NR}_4)$ (PEVP-Br)
1606, 1518	$\nu(\text{C}=\text{C})$ (benzene ring of MO)
1596, 1520	$\nu(\text{C}=\text{C})$ (benzene ring of MY)
1571	$\nu(\text{C}=\text{N})$ (PEVP-Br)
1220–1114	$\nu(\text{S}=\text{O})$ (MY)
1230–1118	$\nu(\text{S}=\text{O})$ (MO)

**TABLE II**  
Attribution of the IR Vibration Peaks

Wavenumber ( $\text{cm}^{-1}$ )	Vibration mode
1726	$\nu(\text{C}=\text{O})$ (PEDEM-MY and PEDEM-MO)
1589, 1535	$\nu(\text{C}=\text{C})$ (benzene ring of PEDEM-MY)
1604, 1521	$\nu(\text{C}=\text{C})$ (benzene ring of PEDEM-MO)
1219–1139	$\nu(\text{S}=\text{O})$ (PEDEM-MY)
1228–1146	$\nu(\text{S}=\text{O})$ (PEDEM-MO)
1640	$\nu(\text{NR}_4^+)$ (PEVP-MY and PEVP-MO)
1589	$\nu(\text{C}=\text{N})$ (PEVP-MY)
1582	$\nu(\text{C}=\text{N})$ (PEVP-MO)
1185–1140	$\nu(\text{S}=\text{O})$ (PEVP-MY)
1189–1116	$\nu(\text{S}=\text{O})$ (PEVP-MO)

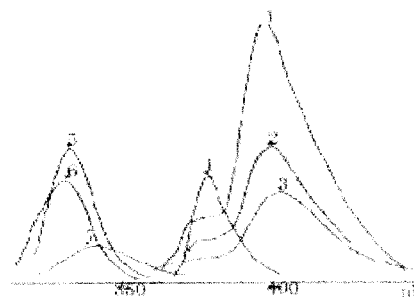
- Scheme 2 shows the syntheses routes of PEVP-Br and its complexes PEVP-MY and PEVP-MO.

### Solubility

The solubility of the complexes is different from that of the polyelectrolytes. It is deduced that almost all the cations are neutralized by the counterions in the dyes, so the whole complexes are hydrophobic and insoluble in water and general organic solvents.<sup>11</sup> The solubility experiment shows that the complexes are partly soluble in alcohol and insoluble in water. Nevertheless, the polyelectrolytes hold good solubility in water and alcohol. The experiment also revealed that the complexes are well soluble in dimethylformamide (DMF).

### FTIR analysis

FTIR analysis was employed to study the complex formation between polyelectrolytes and dyes. In Figure 1, curves 1 and 2 represent the IR spectra of PEDEM-Br and PEVP-Br, respectively. The molecular structure of PEDEM-Br and PEVP-Br reveals that  $1729 \text{ cm}^{-1}$  is the vibration of  $\text{C}=\text{O}$  and  $1655 \text{ cm}^{-1}$  is the vibration of  $\text{NR}_4$  for PEDEM-Br. Respectively, 1644 and  $1571 \text{ cm}^{-1}$  refer to the vibration of  $\text{NR}_4$  and  $\text{C}=\text{N}$



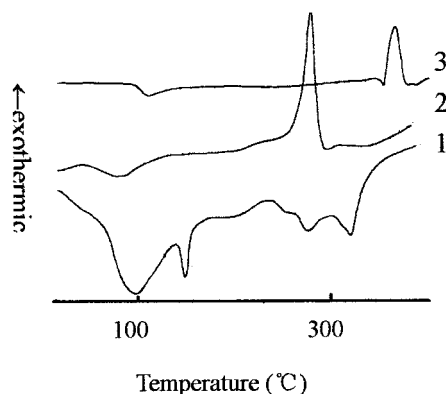
**Figure 2** Fluorescence spectra of samples: (1) MO; (2) PEVP-MO; (3) PEVP-Br; (4) PEVP-MY; (5) PEDEM-MY; (6) PEDEM-MO; (7) MY. Solvent: alcohol.

**TABLE III**  
Excitation Wave and Emission Wave of Samples

Sample	$\lambda_{\text{Ex}}$ (nm)	$\lambda_{\text{Em}}$ (nm)
MY	230–300	340
MO	290–330	395
PEDEM–Br	–	–
PEDEM–MY	270–330	333
PEDEM–MO	230–260	330
PEVP–Br	300–350	405
PEVP–MY	330–335	375
PEVP–MO	270–330	400

for PEVP–Br, as shown in Table I. Curves 3 and 4 (Fig. 1) represent the IR spectra of MY and MO. Characteristic peaks of the S=O group for MY and MO are at  $1220\text{--}1114\text{ cm}^{-1}$  and  $1230\text{--}1118\text{ cm}^{-1}$ , respectively, as shown in Table I.

Curves 5–8 (Fig. 1), respectively, display the IR spectra of the complexes PEDEM–MY, PEDEM–MO, PEVP–MY, and PEVP–MO. For the four complexes, a strong decrease in the quaternary ammonium salt absorption near  $1655, 1644\text{ cm}^{-1}$  is diagnostic, as shown in Table II. Residual quaternary ammonium salt absorption also remains, indicating that complexation is not 100% completely pure. Under the formation of electrostatic force, the bond of C=N for PEVP–Br shifts to higher frequencies. This effect is a consequence of changes in the electronic distributions in the pyridine ring due to the formation of stronger bonds. The most affected bands are presented in more detail in Tables I and II. Pure PEVP–Br has an absorption band at  $1571\text{ cm}^{-1}$ , and this band shifts to  $1589, 1582\text{ cm}^{-1}$  due to the formation of electrostatic interaction. The same changes can be observed in the bond regions of S=O, for MY and MO as they shift to lower frequencies for the same reasons, as shown in Tables I and II. The results strongly indicate evidence that complexation between polyelectrolytes and dyes indeed takes place.



**Figure 3** DTA curves of (1) PEDEM–Br, (2) PEDEM–MY, and (3) MY.

**TABLE IV**  
Transition Temperature of the Samples

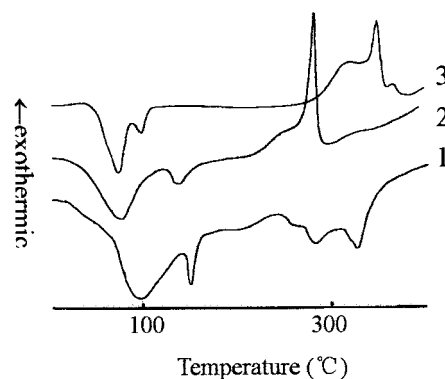
Sample	$T_g$ (°C)	$T_d$ (°C)
MY	115.0*	367.5
MO	70.0*	337.0
PEDEM–Br	87.5	326.5
PEDEM–MY	72.5	284.0
PEDEM–MO	65.0	275.0
PEVP–Br	87.0	390.2
PEVP–MY	62.5	257.5
PEVP–MO	75.0	248.5

The temperatures marked by an asterisk refer to the small molecule's melting temperature.

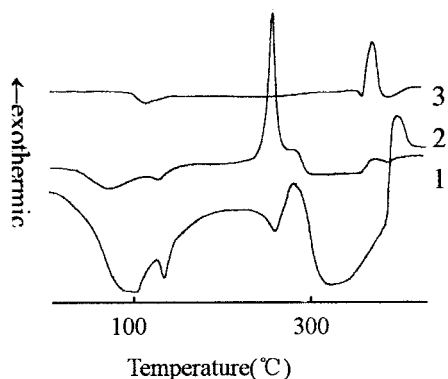
### Fluorescence analysis

The molecules which have a rigid and plane conjugated structure always emit fluorescence, and the maximum emission wave will display a red-shift when conjugation and flatness increase; otherwise, it will show a blue-shift. Figure 2 shows the fluorescence spectra of the samples in alcohol. The sample PEVP–Br has a pyridine ring which makes it display fluorescence. Its maximum emission wave  $\lambda_{\text{Em}}$  equals 405 nm as shown in Table III. For the same reason, MY and MO also present  $\lambda_{\text{Em}}$  (340 nm) and  $\lambda_{\text{Em}}$  (395 nm). When they are assembled with PEDEM–Br and PEVP–Br, the complexes show different  $\lambda_{\text{Em}}$  due to the formation of electrostatic force and hydrophobic interaction. For example, the  $\lambda_{\text{Em}}$  of pure MY is 340 nm and pure PEDEM–Br cannot emit fluorescence without a conjugated structure, but the complex PEDEM–MY shows fluorescence, whose  $\lambda_{\text{Em}}$  shifts to 333 nm. The  $\lambda_{\text{Em}}$  of the complex PEVP–MY has red-shifted to 375 nm in comparison with pure MY, as shown in Table III.

It can be deduced that the molecular variance of the two polyelectrolytes causes the difference between the two complexes. Similar phenomena of the complexes



**Figure 4** DTA curves of (1) PEDEM–Br, (2) PEDEM–MO, and (3) MO.



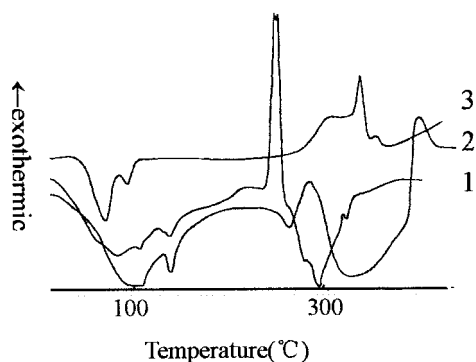
**Figure 5** DTA curves of (1) PEVP-Br, (2) PEVP-MY, and (3) MY.

PEDEM-MO and PEVP-MO in comparison with MO can be observed in Table III.

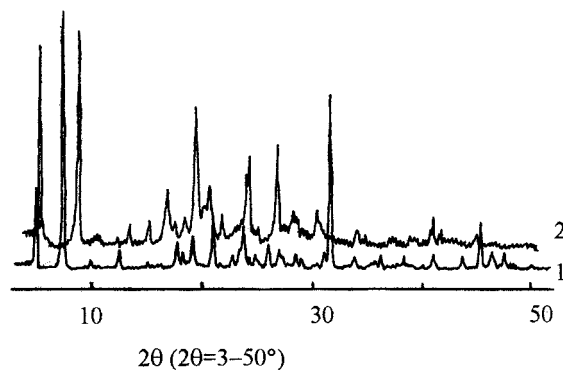
#### DTA analyses

To study the structure change of the complexes, the glass temperature ( $T_g$ ) and decomposition temperature ( $T_d$ ) were investigated by DTA curves. Figure 3 shows the thermograms of the complex PEDEM-MY and pure PEDEM-Br and MY. PEDEM-MY has two transitions at 72.5 and 284°C, as shown in Table IV. It can be inferred that the complex is stable below the temperature of 280°C.

Figures 4–6, respectively, show the thermograms of the different complexes, polycations, and dyes. It is noteworthy that the curves of the four complexes are very similar. The difference is caused by the dyes. The most affected changes are presented in more detail in Table IV. The transition temperatures of the complexes are lower than are the corresponding polyelectrolytes, which is probably the reason that the organic small molecule makes the branched chain of the macromolecular more flexible. Also, it is true that the



**Figure 6** DTA curves of (1) PEVP-Br, (2) PEVP-MO, and (3) MO.



**Figure 7** X-ray diffraction spectra of (1) MY and (2) MO.

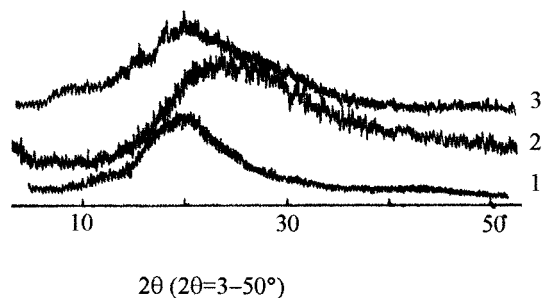
complexes are stable enough to endure high temperature of at least 230°C.

#### X-ray diffraction analyses

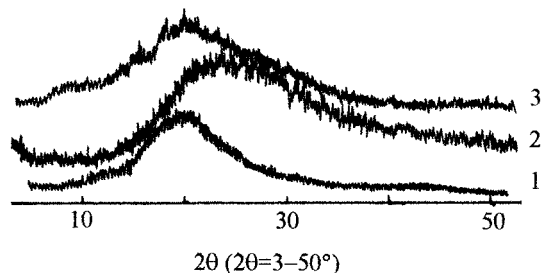
X-ray diffraction analyses were performed to detect the structure of the complexes in the solids. As shown in Figure 7, it is obvious that MY and MO are typical organic crystals, which have several sharp and strong diffraction peaks. PEDEM-Br and PEVP-Br are typical noncrystal polymers which only have a low and dispersive peak (Figs. 8 and 9). The wide-angle diffractograms of the complexes PEDEM-MY and PEDEM-MO consist of a broad halo ( $2\theta = 18^\circ$ ), corresponding to a Bragg spacing of about 0.49 nm, and of the complexes PEVP-MY and PEVP-MO ( $2\theta = 20^\circ$ ), corresponding to a Bragg spacing of about 0.44 nm, which is close to the value of 0.43 nm known for the lateral packing of alkyl chains of surfactants, of which the number of carbons is more than 12.<sup>12</sup> This indicates that only a short-range order is presented in the lateral packing of the complexes.

#### CONCLUSIONS

Four complexes based on PEDEM-Br, PEVP-Br, MY, and MO were prepared and shown to be soluble in some solvents (e.g., DMF). The FTIR results suggest



**Figure 8** X-ray diffraction spectra of (1) PEDEM-MY, (2) PEDEM-Br, and (3) PEDEM-MO.



**Figure 9** X-ray diffraction spectra of (1) PEVP-MY, (2) PEVP-Br, and (3) PEVP-MO.

that complexation between polycations and dyes was achieved. Intermolecular bonds in the complexes are of electrostatic force and hydrophobic interaction without formation of a covalent bond. Four complexes are stable under the temperature of 200°C. The results of the fluorescence analyses proved that the four complexes are new materials formed through an intermolecular weak force. It can be verified by X-ray diffraction analyses that the complexes are mainly amorphous and only short-range order is presented in the lateral packing of the complexes.

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## References

1. Wang, K. *Chem Commun* 1997, 1-6.
2. Lehn, J. M. *Angew Chem Int Ed Engl* 1990, 29, 1304-1309.
3. Khokhlov, A. R. *World Polymer Congress 98*, (preprints); p 5.
4. Lee, K. Y.; Jo, W. H.; Kwom, I. C.; Kim, Y. H.; Jeong, S. Y. *Macromolecules* 1998, 31, 378-383.
5. Asanuma, H.; Ban, T.; Gotoh, S.; Hishiya, T.; Komiyama, M. *Macromolecules* 1998, 31, 371-373.
6. Libert, L.; Marechal, E. *Eur Polym J* 1980, 16, 1211.
7. Guthrie, J. T. *Rev-Prog Colon* 1990, 20, 40.
8. Ober, C. K.; Wegner, G. *Adv Mater* 1997, 9, 18.
9. Creutz, S.; Teyssie, P.; Jerome, R. *Macromolecules* 1997, 30, 6-9.
10. Yang, M.; Li, J.; Qi, Z. *Poly Mater Sci Eng* 1999, 15, 34.
11. Bakeev, V. N.; Yang, M.; Zezin, A. B. *Dokl Akad Nauk (Russ)* 1993, 332, 451.
12. Antonietti, M. *Macromolecules* 1994, 27, 6007.
13. Norwood, D. P.; Minatti, E.; Reed, W. F. *Macromolecules* 1998, 31, 2957-2956.
14. Antonietti, M. *Macromol Chem Phys* 1996, 197, 2713-2727.
15. Fundin, J.; Hansson, P.; Brown, W.; Lidgran, I. *Macromolecules* 1997, 30, 1118-1126.
16. Bazuin, C. G.; Tork, A. *Macromolecules* 1995, 28, 8877.