

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

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ABSTRACT: Four polyelectrolyte complexes were formed through the 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-shift in comparison with those of dyes in alcohol, and the emission waves of the PEVP-MY and PEVP-MO complexes in alcohol were red-shift in comparison with those of dyes in alcohol. The structure of the complexes in solid state were also investigated by differential thermal analysis (DTA) and X-ray diffraction experiments. It was proved that the complexes were new materials formed through weak interactions. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 85: 638–644, 2002

Key words: self-assembly; polyelectrolyte complex; electrostatic force; FTIR; X-ray; self-assembly

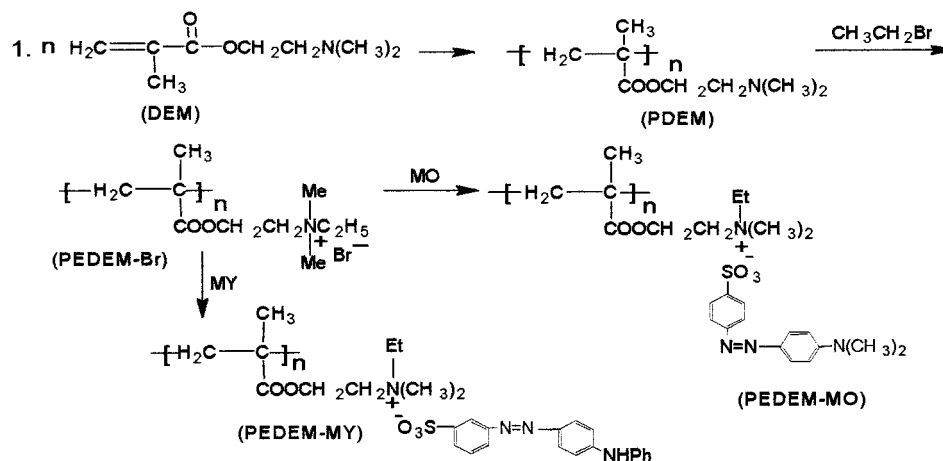
INTRODUCTION

Supramolecular chemistry has been an important field in the development of chemistry since the French scientist J. M. Lehn first defined the conception in his acceptance speech when he won the Nobel prize.^{1,2} In polymer science, polyelectrolytes are always chosen as the model in the studies on supramolecular assembly for the following reasons:³ First, polyelectrolytes have special molecular frameworks and a high sensitivity to exterior condition change. Second, they have plenty of frame forms in a nanometer microcosmic scale and can vary with changes in the parameters of the microcosmic circumstance. Third, almost all

important biologic macromolecules such as poly(peptide), polysaccharides, DNA, and so forth, are polyelectrolytes. Studies of the supramolecular assembly of polyelectrolytes can also provide some help in explaining special life-function courses.^{4,5} Different complexes can be formed through different polyelectrolytes assembled with different surfactants or dyes. The complexes can be used in dyeing, liquid crystal displays (LCDs), nonlinear optics, food, medicine, chromatograms, and other new technical fields.^{6,7} There are fewer studies of supramolecular assemblies of polycations than there are of other polyelectrolytes because it is difficult to acquire the supramolecular assemblies. Polycations such as poly(N-alkylvinylpyridine), lonene-n,n, polyviologen, polyaniline, and polypyrrole have been reported in the literature.⁸ In this article, the bromine salt form of poly-N-ethyl-N,N-dimethylamino ethyl methacrylate (PEDEM-Br) was first

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Scheme 1

used to assemble a polyelectrolyte cation template with dyes, and poly-*N*-ethyl-4-vinylpyridinium bromine salt (PEVP-Br) had also been used to assemble a template with dyes. Studies of 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, differential thermal analysis (DTA) and X-ray diffraction techniques had also been 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), 4-vinylpyridine (VP; chemical pure). The dyes were methyl orange (MO) and

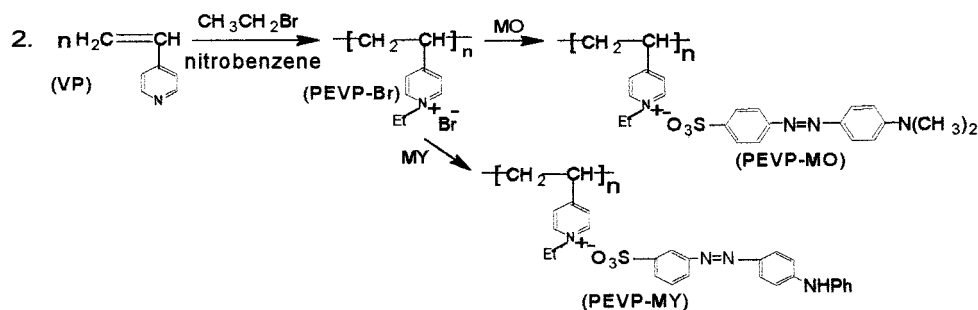
metanil yellow (MY). The solvents included NaOH, tetrahydrofuran, ethyl acetate, bromoethane, nitrobenzene, ammonium peroxydisulfate, and sodium hydrogen sulfite (NaHSO₃). The dyes and solvents listed above were analytically pure (Beijing Chemical Co., Beijing, China).

Measurements

A Nicolet 1700SX FTIR (all samples grounded in KBr), a Hitachi 850 fluorescence apparatus (< 1wt% concentration in alcohol), a Shanghai CDR-1 DTA apparatus (samples were powders and were protected by nitrogen with a velocity of flow was 40 mL/min; the scanning speed was 10°C/min), and a D/max-ra X-ray diffraction apparatus were employed.

Sample Preparation

In a 250-mL three-necked reaction vessel, we mixed 20 mL DEM (which must be purified through distillation before being used), 0.84 g



Scheme 2

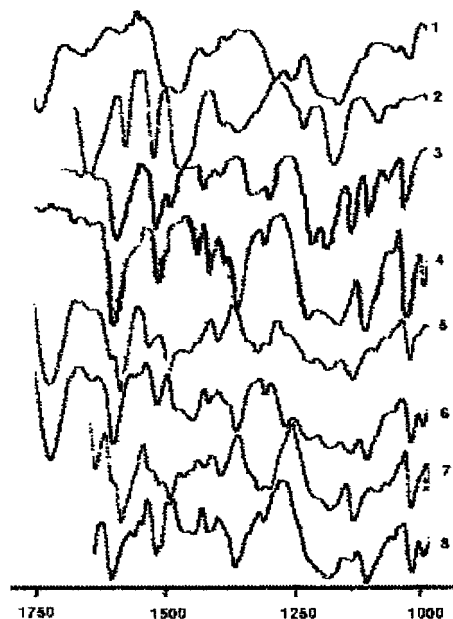


Figure 1 Infrared spectra of samples. 1 = PEDEM-Br, 2 = PEVP-Br, 3 = MY, 4 = MO, 5 = PEDEM-MY, 6 = PEDEM-MO, 7 = PEVP-MY, 8 = PEVP-MO.

(NH_4)₂S₂O₈, 1.68 g NaHSO₃, and 100 mL H₂O and then heated the mixture to 70°–90°C for 7 hr while agitating it. After that, the white suspension could be observed. Then the solution was cooled to room temperature until it became transparent. We then added NaOH aqueous solution (25% w/w) drop by drop until the white precipitation did not increase further. The precipitation was washed several times by highly pure water, and it was put in a vacuum for 48 hr. The product was poly-N,N-dimethylamino ethyl methacrylate (PEDEM).

Excessive bromoethane was added into a 5 wt% solution of PEDEM in THF, then kept agitating at 40°C for 12 hr with the protection of N₂. The final product was recovered by the complete removal of the solvent and the excessive alkyl halide, and this product was put in the vacuum for 2 days. The product was poly-N-ethyl-N,N-dimethylamino ethyl methacrylate bromine salt (PEDEM-Br), with an inherent viscosity of 590.5 (mL/g) in water, determined by a Ubbelohde viscometer at 25°±0.1°C.⁹

The VP was purified by a reducing pressure distillation before use. The 5.72 mol/L solution of the VP was prepared in nitrobenzene, the same concentration bromoethane was also prepared in nitrobenzene. An identical amount of the two solutions was added into ampoule vessel, which was then sealed after the air in it had been expelled by

N₂. After that, the ampoule vessel was put into hot water (50°–60°C) for 3 days. The product was washed and precipitated by ethyl acetate. The precipitation was dried in a vacuum for 48 hr: The final product was poly-N-ethyl-4-vinylpyridinium bromine salt (PEVP-Br),¹⁰ with an inherent viscosity of 142.2 (mL/g) in water at 25°±0.1°C.¹⁰

The same concentration (Br, PEVP-Br, MY, and MO) were prepared. Then the PEDEM-Br solution was added into 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 vacuum for 48 hr. 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 these complexes was approximately 1 : 0.8 (poly-electrolyte 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, including AgNO₃, PEDEM-Br, and PEVP-Br, were prepared in certain concentrations. The AgNO₃ solution was added into the PEDEM-Br solution drop by drop, with the K₂CrO₄ solution as an indicator. The end-point occurred 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 routes of synthesis of PEDEM-Br and the complexes PEDEM-MY and PEDEM-MO are

Table I Attribution of the Infrared Vibration Peaks

Wavenumber (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)

PEDEM-Br = poly-N-ethyl-N,N-dimethylamino ethyl methacrylate (bromine salt form); PEVP-Br = poly-N-ethyl-4-vinylpyridinium (bromine salt form); MO = methyl orange; MY = metanil yellow.

Table II Attribution of the Infrared Vibration Peaks

Wavenumber (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)

PEDEM-Br = poly-N-ethyl-N-dimethylamino ethyl methacrylate (bromine salt form); PEVP-Br = poly-N-ethyl-4-vinylpyridinium (bromine salt form); MO = methyl orange; MY = metanil yellow.

shown in Scheme 1. Scheme 2 shows the synthesis routes of the PEVP-Br and its complexes, PEVP-MY and PEVP-MO.

Solubility

The solubility of the complexes is different from that of the polyelectrolytes. We deduce that almost all cations are neutralized by the counterions in the dyes, so the whole complexes appear hydrophobic and are insoluble in both water and in general organic solvents.¹¹ The solubility experiment shows that the complexes are partly soluble in alcohol and insoluble in water. Nevertheless, the polyelectrolytes have good solubility in water and alcohol. The experiment also reveals that the complexes are highly soluble in dimethylformamide (DMF).

FTIR Analysis

FTIR analysis was employed to study the formation of the complexes between polyelectrolytes

and dyes. In Figure 1, curves 1 and 2 represent the infrared (IR) spectra of PEDEM-Br and PEVP-Br, respectively. The molecular structures of PEDEM-Br and PEVP-Br reveal that 1729 cm⁻¹ is the vibration of C=O and that 1655 cm⁻¹ is the vibration of NR₄ for PEDEM-Br. Respectively, 1644 cm⁻¹ and 1571 cm⁻¹ refer to the vibration of NR₄ and C=N for PEVP-Br, as shown in Table I. Curves 3 and 4 in Figure 1 represent the IR spectra of MY and MO. Respectively, 1220–1114 cm⁻¹ and 1230–1118 cm⁻¹ are characteristic peaks of the S=O group for MY and MO, as shown in Table I.

Curves 5, 6, 7, and 8 in Figure 1 display the IR spectra of the complexes PEDEM-MY, PEDEM-MO, PEVP-MY, and PEVP-MO, respectively. For the four complexes, the strong decrease in the quaternary ammonium salt absorption near 1655 and 1644 cm⁻¹ is diagnostic, as

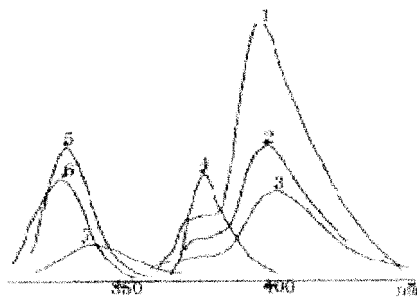


Figure 2 Fluorescence spectra of samples. 1 = MO, 2 = PEVP-MO, 3 = PEVP-Br, 4 = PEVP-MY, 5 = PEDEM-MY, 6 = PEDEM-MO, 7 = MY * solvent: alcohol.

Table III Excitation Wave and Emission Wave of Samples

Sample	λ_{Ex} (nm)	λ_{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

PEDEM-Br = poly-N-ethyl-N-dimethylamino ethyl methacrylate (bromine salt form); PEVP-Br = poly-N-ethyl-4-vinylpyridinium (bromine salt form); MO = methyl orange; MY = metanil yellow.

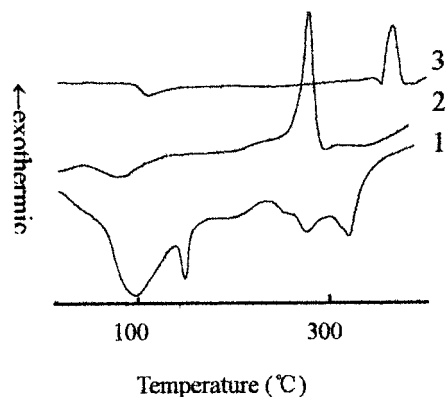


Figure 3 DTA curves of 1 = PEDEM-Br, 2 = PEDEM-MY, 3 = MY.

shown in Table II. Residual quarternary ammonium salt absorption remains, indicating that complexing is not completely pure. Under the formation electrostatic force, the C=N bond for PEVP-Br shifts to higher frequencies. This effect is a consequence of changes in the electronic distributions in the pyridine ring resulting from the formation of more 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 cm^{-1} , and this band shifts to 1589 and 1582 cm^{-1} of formation electrostatic interacting. 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 reason, as shown in Tables I and II. The results strongly indicate that complexing between polyelectrolytes and dyes indeed take place.

Table IV Transition Temperature of the Samples

Sample	Tg (°C)	Td (°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

* Small molecule's melting temperature.

PEDEM-Br = poly-N-ethyl-N,N-dimethylamino ethyl methacrylate (bromine salt form); PEVP-Br = poly-N-ethyl-4-vinylpyridinium (bromine salt form); MO = methyl orange; MY = metanil yellow.

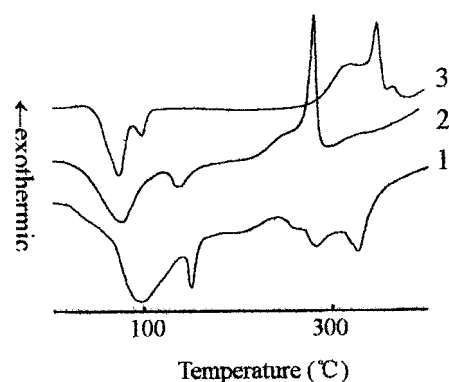


Figure 4 DTA curves of 1 = PEDEM-Br, 2 = PEDEM-MO, 3 = MO.

Fluorescence Analysis

Molecules that have rigid and plane conjugated structures 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 samples in alcohol. The sample PEVP-Br has a pyridine ring, which makes it display fluorescence. Its maximum emission wave γ_{Em} equals 405 nm, as shown in Table III. For the same reason, MY and MO also present γ_{Em} (340 and 395nm, respectively). When they are assembled with PEDEM-Br and PEVP-Br, the complexes show different γ_{Em} as a results of the formation of electrostatic force and hydrophobic interaction. For example, the γ_{Em} of pure MY is 340 nm, and pure PEDEM-Br can not emit fluorescence without a conjugated structure, but the complex PEDEM-MY shows fluorescence with γ_{Em} shifts to 333 nm. The γ_{Em} of the complex

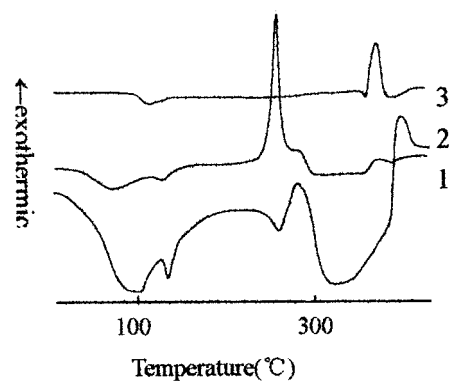


Figure 5 DTA curves of 1 = PEVP-Br, 2 = PEVP-MY, 3 = MY.

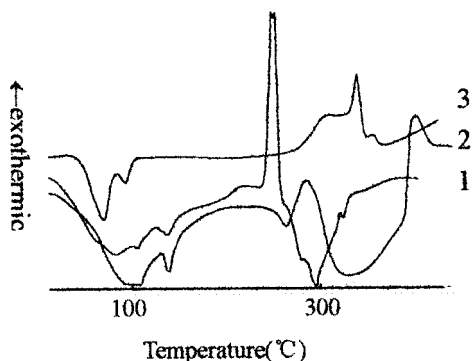


Figure 6 DTA curves of 1 = PEVP-Br, 2 = PEVP-MO, 3 = MO.

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 makes the difference between the two complexes. The similar phenomena of the complexes 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, glass transition temperature (T_g) and decomposition temperature (T_d) were investigated using DTA curves. Figure 3 shows the thermograms of the complex PEDEM-MY and of pure PEDEM-Br and MY. PEDEM-MY has two transitions at 72.5°C and 284°C, as shown in Table IV. It can be inferred that the complex is stable under 280°C.

Figures 4, 5, and 6 show the thermograms of the different complexes, polycations, and dyes, respectively. It is worth noting that the curves of the four complexes are very similar. The differ-

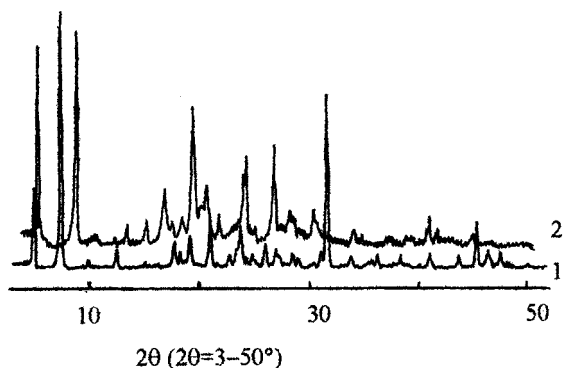


Figure 7 The X-ray diffraction spectra of 1 = MY, 2 = MO.

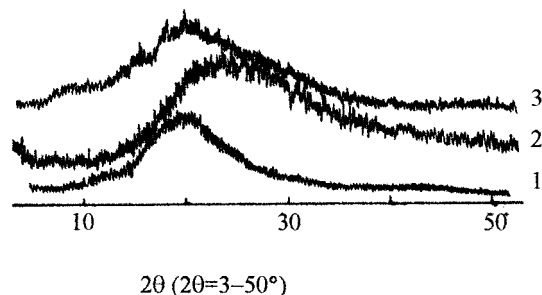


Figure 8 The X-ray diffraction spectra of 1 = PEDEM-MY, 2 = PEDEM-Br, 3 = PEDEM-MO.

ence is caused by dyes. The most affected changes are presented in more detail in Table IV. The transition temperatures of the complexes are lower than those of the corresponding polyelectrolytes, which is probably a result of the fact that the organic small molecule make the branched chain of the macromolecular more flexible. And it is true that the complexes are stable enough to endure high temperatures (at least 230°C).

X-Ray Diffraction Analyses

X-ray diffraction analyses were performed to detect the structure of the complexes in solid form. 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 that only have a single 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 ($2\theta=18^\circ$), which corresponds to a Bragg spacing of about 0.49 nm, and 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 that is known for the lateral packing of alkyl chains of

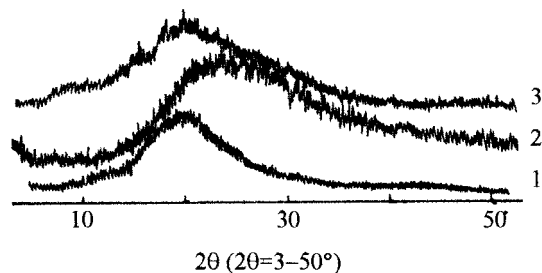


Figure 9 The X-ray diffraction spectra of 1 = PEVP-MY, 2 = PEVP-Br, 3 = PEVP-MO.

surfactants for which the carbon number is greater than 12.¹² This indicates that only a short-range order is presented in the lateral packing of complexes.

CONCLUSION

Four complexes based on PEDEM-Br, PEVP-Br, MY, and MO have been prepared and shown to be soluble in some solvents (e.g., DMF). FTIR results suggest that complexing between polycations and dyes is achieved. Intermolecular bonds in the complexes are electrostatic force and hydrophobic interaction without formation of covalence bond. Four complexes are stable under 200°C. The results of the fluorescence analyses have proved that the four complexes are new materials formed through weak intermolecular force. It can be verified using X-ray diffraction analyses that the complexes are mainly amorphous and that only a short-range order is presented in the lateral packing of complexes.

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