Formation of fractals by the self-assembly of interpolymer adducts of polymethacrylic acid with complementary polymers in aqueous solution

KANDHASAMY DURAI MURUGAN, ARLIN JOSE AMALI and
PARAMASIVAM NATARAJAN*

National Centre for Ultrafast Processes, University of Madras, Taramani Campus, Chennai 600 113, India
e-mail: pnatrajan@hotmail.com

Abstract. Interpolymer adducts of poly(methacrylic acid), (PMAA), with poly(vinylpyrrolidone) in presence of sodium chloride or potassium chloride form highly ordered fractal patterns in films on glass surface on drying at ambient temperature. The structure, morphology and the conditions under which the formation of fractal patterns occurs were investigated by SEM, EDX and confocal microscopic techniques. Self-organization of PMAA with complementary polymers such as poly(vinylpyrrolidone) is well-known and in the presence of sodium chloride formation of the fractals in films of the adducts is a novel observation. Fractal formation occurs due to the aggregation of interpolymer adducts. The composition of the fractals in the film is studied by EDX and confocal microscopic images of the fluorophores covalently bound to PMAA. In presence of salts, sodium chloride or potassium chloride, micellar like entities of 80 nm size were formed which further aggregate to form fractal patterns. It is suggested that the fractals result from the interpolymer adduct by Diffusion Limited Aggregation mechanism.

Keywords. Fractal; polyelectrolytes; self-organization; thin films; SEM; confocal microscopy.

1. Introduction

Structurally organized nanoscale and microscale films are considered to be important in nanotechnology applications for molecular electronics, photonics, photovoltaics and multifunctional nano-devices.[1–4] Self-organizing chemical and biological systems with inorganic molecules, peptides, functionalized carbon nanotubes, polymer composites and hydrogels are known to form fractal structures.[5–10] Fractal structures are predominantly produced due to the self-assembly of molecular and supramolecular systems. Both synthetic and biological macromolecules with fractal structures offer immense scope for material processing from micro to lower end nanometer dimensions.

Polycarboxylic acids form self-organized polymeric adducts with complementary synthetic polymers through hydrogen bonding (scheme 1) and its properties, composition and structural features have been studied extensively.[11] The structure of self-organized macromolecular adduct systems has been studied using spectroscopic, chemical and microscopic methods.[12,13]

In aqueous solution, interpolymer adducts are known to form micellar-like entities depending on pH of the solution, substituents in the polymer chain and the ionic environment. The structural features and the formation of the interpolymer adducts have been investigated extensively using fluorophores covalently attached to the polycarboxylic acid systems.[13] The stability of the interpolymer adducts depends on the extent of hydrogen bonding, hydrophobic interaction and other non-covalent interactions. PMAA has the tendency to form more stable interpolymer complexes as compared to PAA due to the α-methyl substituent present in PMAA chain. In the present investigation, we report the novel observation of the formation of fractal patterns in self-organizing polyacrylic acid systems in films driven by hydrogen bonding and other non-covalent interactions. Our earlier studies provide details on the adduct formation between polyacrylic acids and complementary polymers using fluorophores covalently bound to polyacrylic acids and by time resolved absorption spectral methods.[14]

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*For correspondence
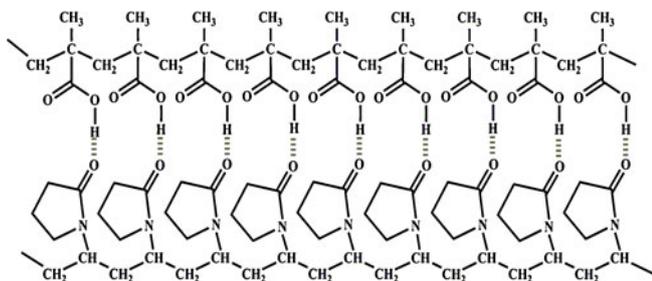
Scheme 1. Structure of interpolymer adduct of poly(methacrylic acid) with poly(vinyl pyrrolidone).

2. Experimental

2.1 *Materials*

Methacrylic acid was purchased from Alfa Easer and vacuum distilled before polymerization. Poly(vinyl-pyrrolidone), (PVP), of molecular weight 25 kD and proflavine were purchased from Fluka. Phenosafranine, poly(ethylene glycol), (PEG), poly(ethylene oxide), (PEO), and poly(vinyl alcohol), (PVA), were obtained from Aldrich chemicals. All other reagents were of analytical grade and used as received. Triply distilled water was used to prepare polymer solutions.

2.2 *Methods*

Polymethacrylic acid was prepared by the free radical polymerization of methacrylic acid in aqueous solution. The polymerization reaction was carried out with 40% aqueous solution of methacrylic acid (30 ml) in presence of potassium persulphate ($\sim 0.1\%$) as radical initiator. As the reaction proceeds, the reaction mixture becomes viscous and the viscous solution was precipitated using 4:1 acetone and petroleum ether mixture as non-solvent. The fluorophores were covalently attached by the condensation of the carboxylic group of the polymer back bone and amino group of the dye through amide linkage as reported earlier.[15] In general, about 500 mg of PAA or PMAA was dissolved in 25 ml water and the dye (proflavine or phenosafranine) was added ($\sim 1\%$ by molar ratio with respect to monomer unit of the polymer solution) and the condensation reaction was carried out at 90°C for 8 h. The sample was purified through the dialysis of the solution against distilled water for weeks using cellulose tube (Sigma-Aldrich, Molecular weight Cutoff -12 kD). During the dialysis the unbound dye was removed from the sample and at the end of the purification process the absorbance of water outside the dialysis tube was checked to confirm that there are no unbound dyes leaching out from the

Table 1. Molecular weights and m/d ratios of the dye bound polymers.

Sample	M_w(kDa)	m/d (± 5)
PMAA	86	—
PMAA-PF$^+$	86	275
PMAA-PS$^+$	91	140

dialysis tube. The amount of dye molecules covalently attached to the polymer backbone was estimated spectrophotometrically. Known amount of polymer bound dye was dissolved in water and the pH of the solution was adjusted to neutral pH by using 0.1 M sodium hydroxide solution. The absorbance of the polymer bound dye solution was measured by UV-visible spectrophotometer and by knowing the molar absorption coefficient of the dye at the spectral maximum (proflavine: $4.1 \times 10^4\,M^{-1}\,cm^{-1}$; phenosafranine: $1.83 \times 10^4\,M^{-1}\,cm^{-1}$), the amount of dye present in the solution was estimated. The molecular weight and monomer unit/dye ratio of the samples are presented in table 1. The structure of the fluorophore bound polymer is shown in scheme 2. For preparing films, polymer solutions (corresponding to 0.01 M monomer) were prepared from the polymer bound with the dye in aqueous solution of pH around 4.5; pH of the solution was adjusted using hydrochloric acid and sodium hydroxide. Interpolymer complexes were formed by mixing of PMAA and its complementary polymers in equal molar ratio; it is known that the interpolymer adducts form with a molar ratio of 1:1 of the polymers.[11] About 60 μl of this solution was placed on a clean glass slide which on evaporation at ambient temperature forms a thin film.
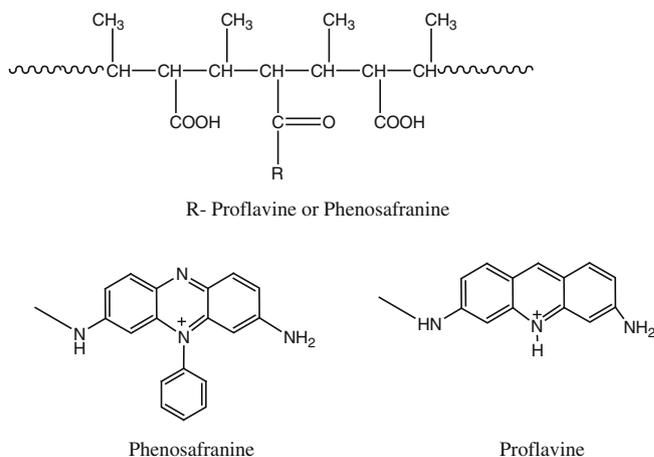
Scheme 2. Structure of fluorophore bound polymethacrylic acid).

2.3 *Measurements*

The absorption spectra of the samples were recorded on an Agilent Diode-Array spectrophotometer. The molecular weights of the samples were determined by using Agilent 1200 high-performance liquid chromatography with Agilent ZORBEX GF- 250 (4.6 mm × 250 mm) column. Polyvinyl alcohol of various molecular weights in phosphate buffer (pH − 7.4) was used as reference. The detection was carried out by making use of UV-Vis Agilent Infinium 1260 Diode Array Detector by measuring the absorbance at 200 nm with micro absorbance unit accuracy. The microscopic images of the film thus formed were recorded using Hitachi scanning electron microscope. The energy dispersive elemental analyses, EDX, of the samples were recorded on Thermo equipment attached with scanning electron microscope. Laser scanning confocal microscopic images were taken using Leica TCS SP2 Laser scanning confocal microscope. Ar-ion laser line at 458 nm was used to excite the polymer bound proflavine samples and He/Ne laser line 543 nm was used in case of phenosafranine samples. Field emission scanning electron microscopic images were recorded by using Quanta LV field emission scanning electron microscope.

3. Results and Discussion

3.1 *Results*

3.1a *Optical and confocal microscopic studies*: Studies on the dynamics of the films of polyelectrolytes and their interpolymer complexes on smooth surfaces provide information on the morphology, self-organization behaviour and orientation of the macromolecular system under various conditions.[16,17] The preparation of films with desired surface morphology and functional moieties is a challenging task which is of current interest. Fabrication of fractal architectures by chemical deposition, electrochemical deposition, micro printing and other methods is known.[8,18,19]
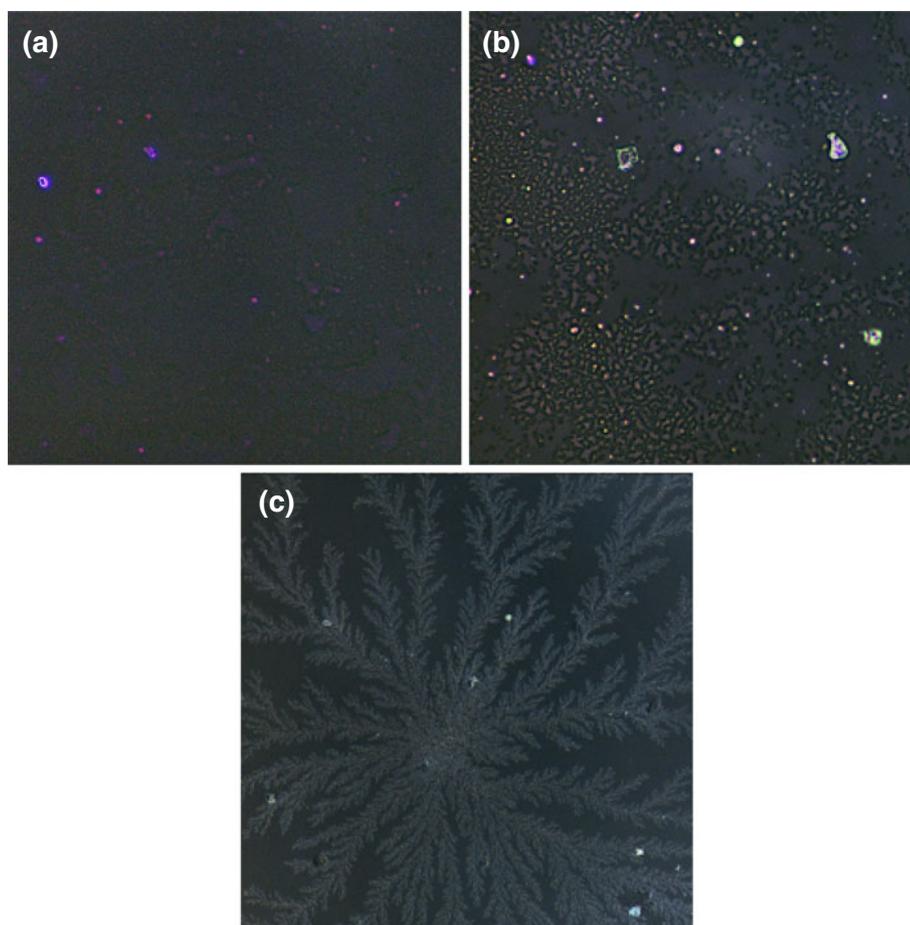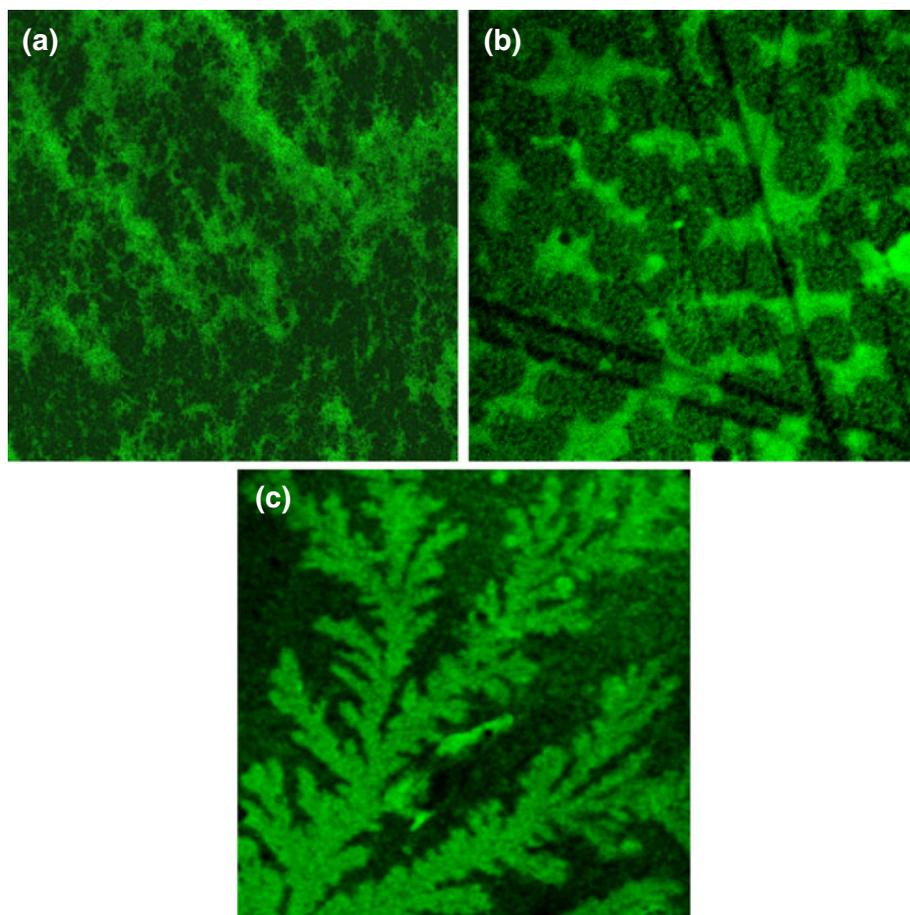

Figure 1. Optical microscopy images of films of the (**a**) PMAA, (**b**) PMAA/PVP interpolymer adduct and (**c**) PMAA/PVP interpolymer adduct (0.01 M NaCl) prepared on glass surface at room temperature (magnification: 20×).

The solvent casting method for the preparation of polymer films is a viable and cost effective method where the solute to be fabricated as thin film is dissolved in a volatile solvent and cast as thin films on the surface of an inert substrate. The solvent is allowed to evaporate under ambient conditions.[20] In the present investigation, an attempt is made to fabricate thin films of the polymer PMAA and its hydrogen bonded interpolymer adduct with complementary polymers on a glass surface and the morphology of the thin films is investigated under various conditions. The inverted optical microscopic image of the thin film of PMAA in aqueous solution at pH − 4.50 is shown in figure 1a. The image shows a uniform morphology over the entire area of the sample. The optical microscopic image of the film of the interpolymer adduct of PMAA with PVP prepared in aqueous solution and evaporated on glass slide is shown in figure 1b which reveals larger aggregate-like structure. For comparison, the optical microscopic image of the film of the adduct of PMAA with PVP prepared in the presence of 0.01 M NaCl is shown in figure 1c. The PMAA/PVP interpolymer adduct film produced in presence of electrolyte shows ordered fractal morphology.

In order to ascertain whether the formation of fractals is due to the self-organization of interpolymer adduct or due to the crystallization of added NaCl, the studies are carried out with PMAA bound with different fluorescent probes. The films are prepared as mentioned earlier for optical microscopy and the images are recorded on exciting the fluorescent probe at the wavelength where the fluorophore absorbs. The fluorescence confocal microscopic images of PMAA and its interpolymer adduct of PVP in the absence and in the presence of NaCl are shown in figures 2(a–c). The morphology of PMAA film prepared in aqueous solution exhibits inhomogeneous distribution of PMAA over the surface. In contrast, the film prepared in 0.01 M NaCl added

Figure 2. Laser scanning confocal microscopic images of films of (**a**) PMAA, (**b**), PMAA/PVP interpolymer adduct and (**c**) PMAA/PVP interpolymer adduct (0.01 M NaCl) prepared on glass surface at room temperature.

to the aqueous PMAA solution at pH − 4.5 and evaporated as thin film on glass plate shows the inhomogeneity of film morphology. Only in the case of film prepared with PMAA/PVP adduct in presence of 0.01 M NaCl in aqueous solution shows the fractal patterns.

3.1b *SEM and EDX measurements*: In order to get more insight on the film morphology at higher resolution and the elemental composition of the film at various positions, the SEM and EDX studies are carried out. The SEM images of the film prepared using PMAA/PVP interpolymer adducts in aqueous solution at pH − 4.5 in the presence of 0.01 M NaCl are shown in figure 3 with varying magnification. The SEM image (figure 3a) observed is found to show similar pattern as observed in the image of laser scanning confocal microscope (figure 2c). At higher magnification, clustering of the polymer complexes are seen (figures 3b and c).

The spherical particles with diameter of ∼ 80 nm are observed at higher magnification as shown in figure 3d.

The SEM images are also recorded for samples prepared at lower concentration of NaCl (0.001 M) and the images are shown in figures 4(a and b). The fractals formed at lower concentration of NaCl is smaller in size compared to that observed using 0.01 M NaCl solution and at higher magnification it is visualized that the NaCl is crystallized as bulk crystals along the fingers of the fractals. However, the fractals are formed only in the case of polymer adducts PMAA/PVP as seen in figure 4b.

The elemental composition of the SEM image is recorded for the whole imaging area and at particular points of interest. The composition of elements present in the film for figure 5a is tabulated in table 2 and the composition at the points marked in the image is also given in table 3. The interpolymer adduct of PMAA with PEO as the complementary polymer in aqueous solution at pH − 4.5 in the presence of 0.01 M
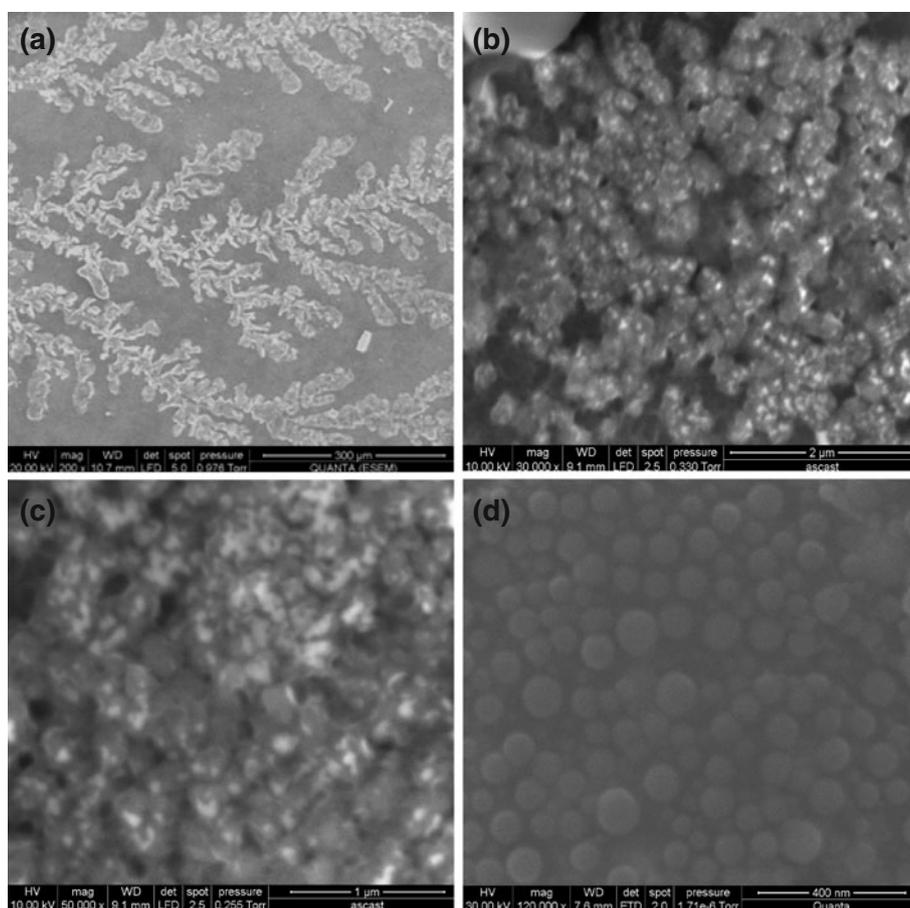
Figure 3. Field emission scanning electron microscopic images of thin films of the PMAA/PVP interpolymer adduct (0.01 M NaCl) prepared on glass surface at room temperature.
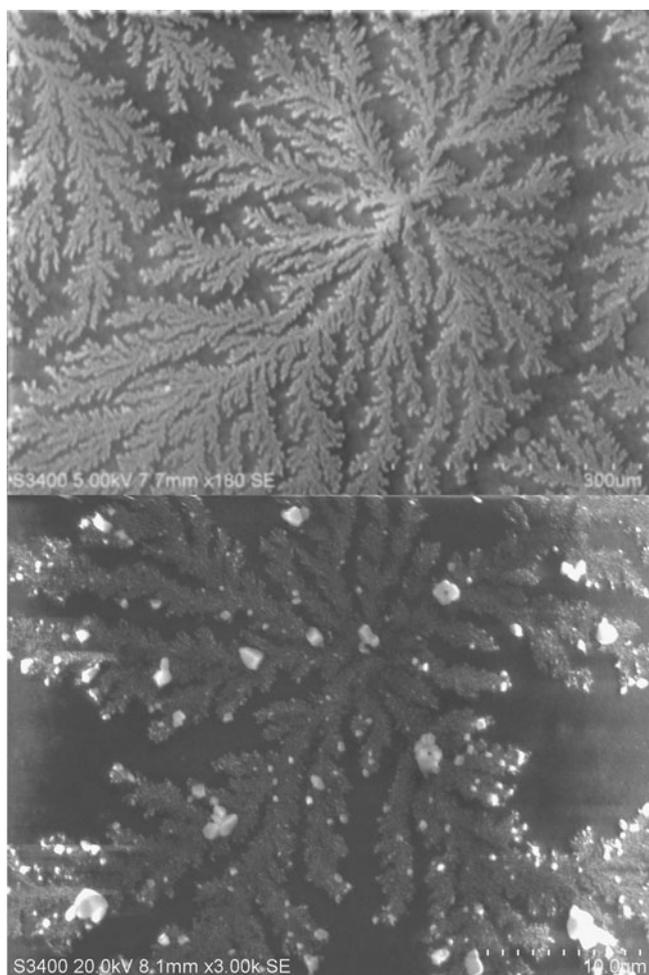
Figure 4. Scanning electron microscopic images of thin films of the PMAA/PVP interpolymer adduct (0.001 M NaCl) prepared on glass surface at room temperature.

NaCl forms a fractal network as observed in confocal and optical microscopic images shown in figure 6. It is also confirmed that PMAA forms fractal pattern with films produced with other complementary polymers such as poly(vinyl alcohol) in aqueous solution at pH − 4.5 ± 0.2.

3.2 *Discussion*

The fractal patterns were observed for the first time in thin films of PMAA containing PVP and other complementary polymers, prepared by the evaporation of the aqueous solution at room temperature. The molar concentration of the monomer units in the polymers is in the range of 10^{-2} M dissolved in 0.05 M sodium chloride at pH − 4.5 ± 0.2. Under similar experimental conditions adducts between poly (acrylic acid), PAA, and PVP in thin films do not form well-defined fractal

structural pattern. The polymers, PMAA, PAA and PVP separately dissolved in aqueous solution and evaporated at room temperature under identical conditions do not form the fractal structural patterns even in the presence of sodium chloride. It is also observed that the fractal pattern is not seen when aqueous solution of the interpolymer adduct has no sodium chloride. Fractal patterns are also produced when sodium chloride is substituted with potassium chloride and such patterns are not observable when phthalate buffer or sodium sulphate is used in the medium; sodium chloride solution alone on evaporation do not show the patterns reported in this study.

Confocal microscopic studies are carried out with the fluorophores, proflavine and phenosafranine, covalently bound to PMAA.[21] The film formation is repeated under identical conditions for the fluorophore bound PMAA/PVP system as detailed above. The confocal microscopic images observed are shown by proflavine as the covalently bound fluorophore which match with those obtained in the SEM. When the covalently bound fluorophore in the PMAA is phenosafranine a similar fractal pattern is observed.

The following conclusions are drawn from the observations. At higher magnification it is seen that the neat spherical patterns of ∼80 nm dimensions are formed from the adduct. The ensembles formed further diffuse during evaporation under the influence of sodium chloride ionic environment to form the fractal aggregated structures. The fractal structures are reproducible even at millimolar concentrations of sodium chloride. At higher concentrations of sodium chloride, the large rectangular crystals of sodium chloride masks the structure of the polymer adduct.

In the recent past, there has been considerable interest in the study of fractals formed by aggregation, self-organization or agglomeration at surfaces.[22] Self-organization process at the molecular level is known to occur predominantly by non-covalent interactions. The critical balance between molecular systems and the conditions of film formation leads to the fractal structures with well-ordered fingers.[10] In the present case which is fairly a simple macromolecular and well-studied system as far as the polymer adduct formation is concerned, the formation of highly ordered fractals could be described as shown in scheme 3. When polymer adducts in aqueous solution evaporated slowly in a two-dimensional quartz or glass or an inert polymer plate the fractals are formed by Diffusion Limited Aggregation (DLA) of the polymer adducts.[23] The formation of the fractal structure is a process far removed from equilibrium aided by the two-dimensional surface and ions present in the solution. The mesoscopic
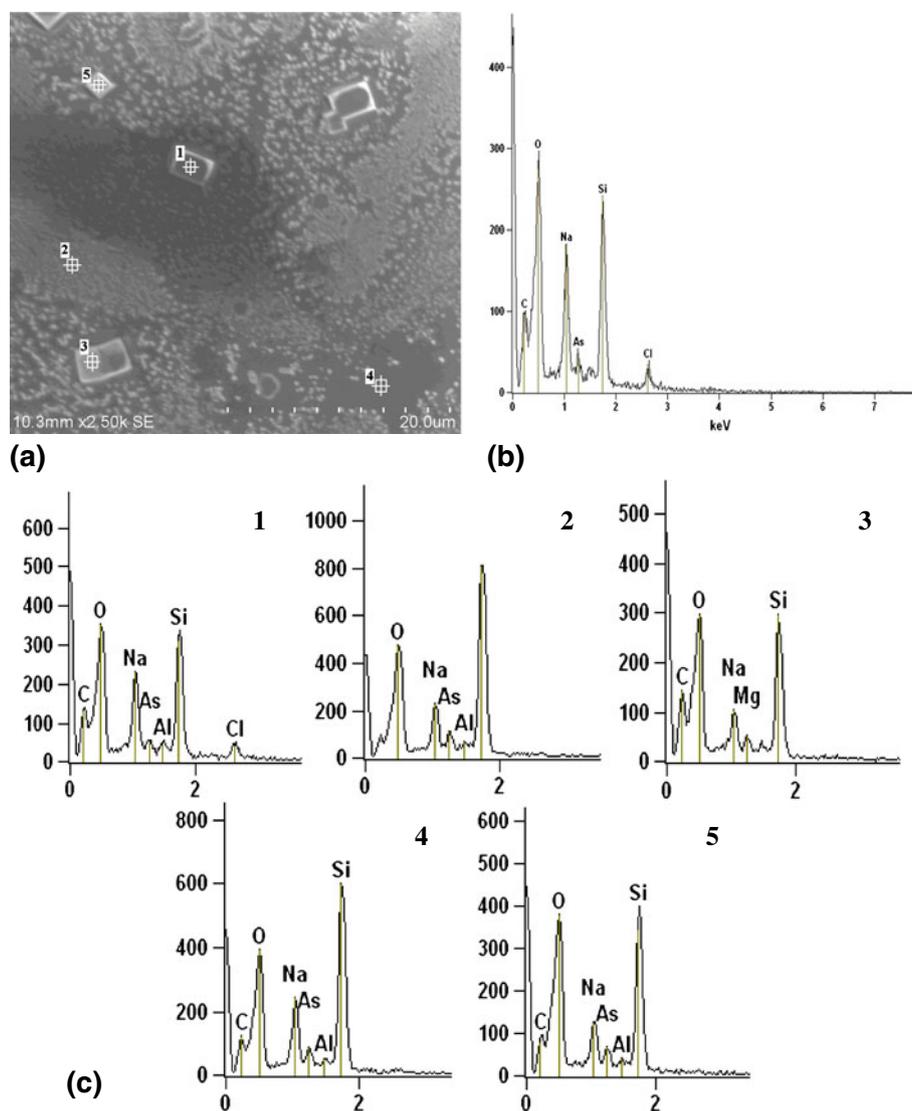
Figure 5. (**a**) The SEM image corresponding to (**b**) the EDX spectrum shown, (**c**) EDX spectra at the respective points marked in the image.

morphology of fractals is determined by the nature of substituents present in the self-organizing system. In the present situation, the hydrophobic effect of the α-methyl substituent in the PMAA segments aid the particular self-organized structure of the polymer adduct leads to the fractal formation.

Based on the observation of the fractal structure at different magnification, we suggest that at low pH (pH < 3.0), in solution globular form of the polymer adduct rapidly nucleates leading to coagulation which in turn precipitates after sometime. It is known that the white precipitate thus formed shows partial crystallinity.[24] At

Table 2. The EDX composition of the film over area of image shown in figure 4.

Element	Net	Weight %	Atom %
C	584	21.91	28.38
O	2375	66.12S	64.30
Na	1364	6.34	4.29
Si	2315	4.88	2.70
Cl	273	0.75	0.33

Table 3. EDX composition of the film at points marked in the image shown in figure 4.

Points	C	O	Na	Cl
1	21.7	66.2	5.6	1.0
2	—	47.9	12.6	—
3	22.8	68.3	3.0	—
4	19.9	65.3	5.1	—
5	19.6	65.5	4.6	—
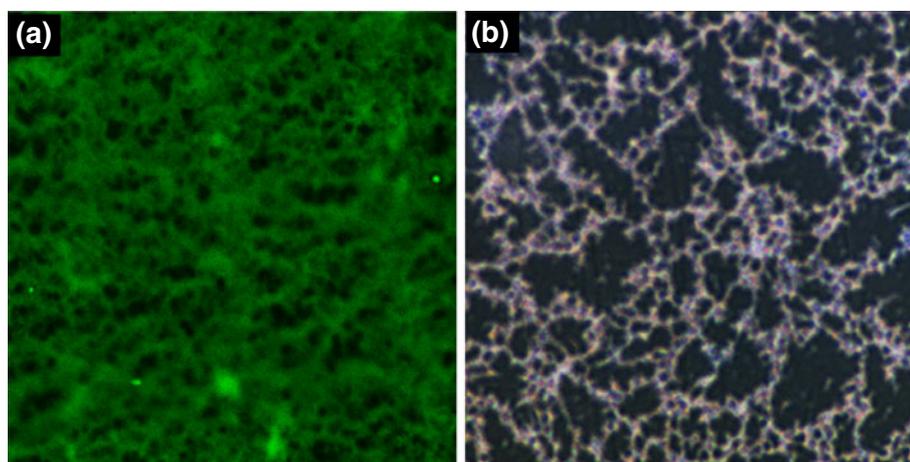
Figure 6. (**a**) Optical and (**b**) Laser scanning confocal microscopic images of PMAA/PEO adduct on glass surface (0.01 M NaCl).

pH $\sim$ 4.5 in aqueous solution, partially ionized PMAA ($\alpha = 0.07$) with complementary polymer forms soluble adduct. Adduct thus formed leads to the formation of micelle-type structure in solution with the micellar core more hydrophobic. It is proposed that this polymer adduct exists as micellar segments in the supramolecular PMAA/PVP adduct formed by hydrogen bonding, hydrophobic interactions and ionic environment.

The fractal dimension is a quantitative parameter which gives information on the mechanistic processes leading to the formation of fractals or the formation of other irregular geometries. The dimension of a fractal could be defined as

$$D_f = \log N(l) \Big/ \log l \to (1),$$

where D_f is the fractal dimension, $N(l)$ is the number of boxes with length 'l'. The fractal dimension is estimated using box counting method. In this approach, the image is converted into a binary image and the image is covered by square boxes that vary in size from 2 to 64 pixels. The number of such boxes, 'N' and their size 'l' are used to compute the fractal dimension using image –J software.[25]

The binary image converted using image-J is shown in figure 7a. The plot of log(N) Vs log(l) is presented in figure 7b. The slope of the plot gives fractal dimension of 1.73 ± 0.02; the fractal dimension for the PMAA/PEO adduct is also calculated and it is found to be 1.72 ± 0.02.

While the detailed structural motifs of polymer adduct in aqueous solution is still not clear, the formation of blobs from such an adduct leads to the globular nature of the adduct leading eventually to form the fractal structure in films. The fractal dimension calculated by box counting method as detailed earlier[23] shows a value of 1.73 ± 0.02. There are many other chemical systems which form fractal structure which show a value of 1.7 which corresponds to a diffusion limited aggregation (DLA), mechanism for the formation of fractal structure.[10] The notable feature of this study is that for the first time we are able to obtain fractal forming self-organizing molecular system involving a polyelectrolyte, PMAA and a complementary polymer PVP. The structural features and conditions under which the fractal structure formation occurs provide valuable information to design nano structures in large scale which are under further investigation.
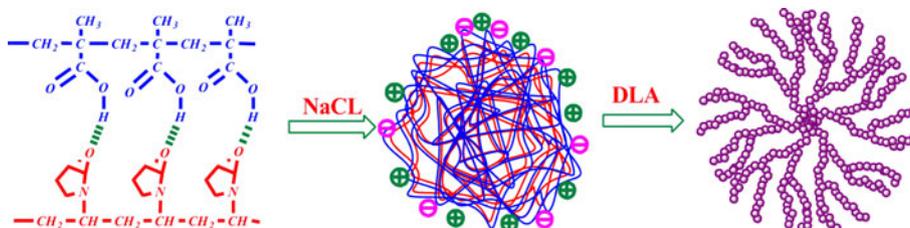
Scheme 3. Formation of fractals through diffusion limited aggregation.
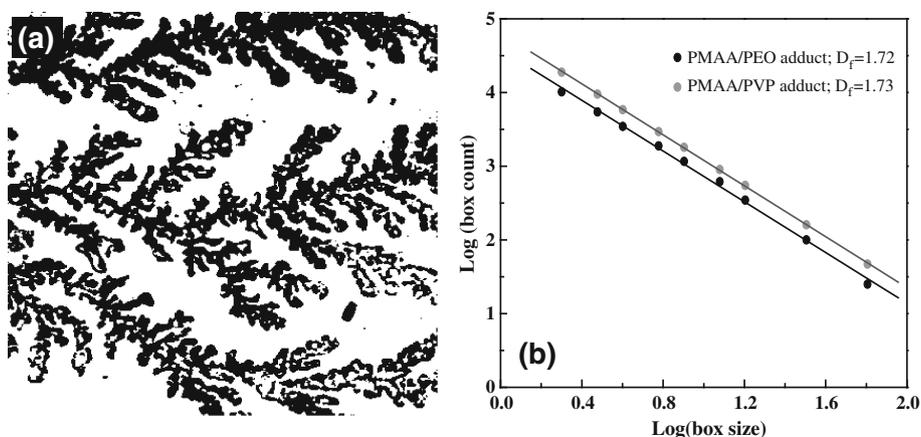
Figure 7. Calculation of fractal dimension. (**a**) Binary image converted using Image J and (**b**) plot of log (box size) Vs log (box count).

4. Conclusion

Fractals with well-ordered structures were fabricated using a simple macromolecular system consisting of PMAA and PVP on glass surfaces in the presence of sodium chloride. The mechanistic details and condition for the formation of fractals are explored using optical and confocal microscopic techniques. The EDX analysis and CLSM images of the fluorophore bound polymer adduct films on glass surface reveals the aggregation of the adducts which leads to formation of fractal structures induced by the sodium chloride present in solution. The aggregated adducts are presumably of 80 nm size formed under the conditions described which on evaporation underwent diffusion limited aggregation driven by hydrophobicity and ionic environment.

Acknowledgements

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