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ORIGINAL CONTRIBUTION

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Conversion of colloidal aggregates into polymer networks on aging

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Abstract After long-term aging, surfactant-mediated colloidal aggregates of sulfonated polyaniline (S-PANI) and poly(vinylidene fluoride) (PVF_2) converted into three-dimensional polymer networks, whereas colloidal crystals prepared from pure PVF_2 remained unaltered. A model, where the surfactant tails anchored from the colloidal particles interdigitate with time resulting in coalescence of the particles to form the network morphology, has been proposed. X-ray photoelectron spectroscopy (XPS) revealed higher relative abundances of carbon atoms on the surface of the polymer networks than those of the colloidal aggregates, which adequately supports the proposed model.

Keywords Sulfonated polyaniline · X-ray photoelectron spectroscopy · Scanning electron microscopy · Colloidal aggregates · Polymer network

Introduction

A colloidal crystal is a three-dimensional ordered arrangement of colloidal particles. Monodisperse silica or polymer latex [1] particles larger than 70 nm in diameter are known to form colloidal crystals [2]. Colloidal crystals have many potential applications such as photonic band-gap materials [3], microchip reactors [4], and size-selective membranes [5]. They are also used in optical switches [6] and in chemical sensors [7, 8]. In addition, they may find applications in catalysis and in separative techniques [9]. Colloidal crystals are usually prepared by gravity sedimentation of the colloids from dispersions [1, 10, 11]. Other methods include: (i) crystallization in capillaries followed by solvent evaporation [12], (ii) spin-coating of colloidal dispersions [13, 14], (iii) capillary force to drive the assembly of colloids [15], and (iv) electrostatic interaction of colloids on vesicle surfaces [16]. The polymer colloidal crystals are usually produced from polymer–surfactant systems through a delicate balance of the attractive and repulsive forces between the surfactant molecules and the polymer chain forming the latex particles [16, 17].

In a recent paper [17] we reported that sulfonated polyaniline (S-PANI) produced colloidal aggregate on didodecyldimethylammonium bromide (DDAB) vesicle surfaces with a particular charge density. Increased charge density on the vesicle surface resulted in the formation of polymer network or a mixture of colloidal aggregate and network. While investigating the above colloidal aggregates preserved in a desiccator over $CaCl_2$ for more than 1.5 months, we observed that the colloidal aggregates had transformed into network. Being curious about this observation, we started investigating this matter and wanted to know whether it is a common phenomenon in surfactant-mediated colloidal aggregates/crystals. So we prepared another system of colloidal aggregate from a very well-known piezoelectric polymer, poly(vinylidene fluoride) (PVF_2) and a surfactant, dodecyl benzenesulfonic acid (DBSA) and to our surprise, we found that these colloidal aggregates also converted into a network morphology on aging. We also prepared colloidal crystals from PVF_2 without using any surfactant, and its morphology did not change with time [18].

Recently, Chen et al. [2] reported that poly(styrene-*co*-2-hydroxyethyl methacrylate) colloidal crystals can be transformed into a net by exposure to styrene or toluene vapor followed by drying. They proposed that the conversion takes place by swelling of styrene in the polystyrene-rich cores of the particles, which expand and engulf the poly(2-hydroxyethyl methacrylate) (PHEMA)-rich shell, leaving the polystyrene-rich phase on the surface and the PHEMA-rich phase inside after drying. X-ray photoelectron spectroscopic (XPS) study showed a higher oxygen content on the surface of the colloidal crystal than that on the network surface.

In this paper we illustrate with the aid of a model that colloidal aggregates involving polymer and surfactants are metastable systems which gradually transform into a network morphology on aging. We have chosen colloidal systems of S-PANI and PVF_2-DBSA as examples and used XPS as the analytical tool.

Experimental

Samples

Polyaniline (PANI) was prepared by polymerizing aniline in hydrochloric acid medium with ammonium persulfate (APS) as initiator [19]. It was converted into the emeraldine base form (EB) by treating with NH_4OH solution. The molecular weight of the polymer was obtained [20] by intrinsic viscosity measurement in sulfuric acid and was found to be 15,500. The PANI (EB) was transformed into leucoemeraldine base (LEB) by mixing with phenyl hydrazine and extracting from its ether solution [21]. The PANI–LEB was sulfonated [21] and converted into its Na salt by dissolving it in 0.1 M NaOH solution, stirring for 2 h and then drying. It was finally dried in vacuum at 60 °C for three days.

Poly(vinylidene fluoride) (PVF_2) was a commercial product of Solvay Corporation, USA (Solvay 1010). It was recrystallized from a 0.3% (w/v) solution in acetophenone (E. Merck, India) and dried in vacuum at 80 °C for four days. The PVF_2 had molecular weight $M_w = 4.48 \times 10^5$, polydispersity index 2.09, and head-to-head defect = 4.19 mol%[22].

The surfactants didodecyldimethylammonium bromide (DDAB) (Fluka, Swizerland), polyoxyethylene(9-10)-*p-tert*-octylphenol (TX-100) (Spectrochem, India), sodium dodecyl sulfate (SDS), and a cosurfactant *n*-octanol (Lanchester, England) were used as received. Dodecyl benzenesulfonic acid (DBSA) was a gift from Dr. P.J. Kinlen, Monsanto Company, St. Louis, USA, and was dried in a vacuum desiccator over $CaCl_2$. Commercial distilled water was redistilled over alkaline potassium permanganate. DMF (E. Merck, India) was dried with $CaSO_4$ and was fractionally distilled at ca. 100 °C under reduced pressure. The middle fraction of the distillate was preserved under a N_2 atmosphere over Linde 4A molecular sieves.

Preparation of colloidal aggregates

Colloidal aggregates of S-PANI

The colloidal aggregates of S-PANI were prepared on vesicle surfaces. A latex of S-PANI was prepared by mixing 1% S-PANI in water with 1% SDS solution in water and standing for two days. Vesicle surfaces were prepared by ultrasonically mixing (30 min) an aqueous solution of DDAB (0.5% w/v), TX-100 (mol fraction = 0.75 with respect to DDAB), and *n*-octanol (weight fraction = 0.35 with respect to TX-100). Colloidal aggregates of S-PANI were produced on these vesicle surfaces by mixing the two solutions together and keeping undisturbed for 24 h. The particles were finally collected by centrifugation (14,000 rpm) at 10 °C and were dried in vacuum at 100 °C for five days.

PVF_2 colloidal aggregates/crystals

The preparation of pure PVF_2 colloidal crystals has been described elsewhere [18]. The PVF_2–DBSA colloidal aggregates were prepared by making a 0.5% (w/v) solution in DMF in a stoppered vessel at 50 °C. An appropriate amount of DBSA from a 1% (w/v) stock solution in DMF was added to the PVF_2 solution to make the weight fraction of DBSA equal to 0.33 in the PVF_2–DBSA blend. It was then stirred for 6 h at 50 °C. Films were cast on 1-cm^2 clean glass slides or on Petri dishes by evaporating the solvent at ca. 50 °C in a gentle pull of air. The samples were finally dried in a vacuum oven for three days at ca. 60 °C.

SEM study

The SEM study of the samples was performed 3 and 45 days after their preparation. The samples were gold-coated and observed at an electron accelerating voltage of 25 kV with the SEM apparatus (Hitachi S-415A). The fresh samples showed a colloidal aggregate morphology whereas the aged samples showed a network morphology.

XPS study

The XPS measurements were done in a UHV–XPS system of M/S Perkin–Elmer, USA, Model 1257 using Mg K_α radiation of 1253.6 eV. The electron energy analyzer was a hemispherical sector analyzer of diameter 279.4 mm with energy resolution capability of 25 MeV. The wide scans were taken with 1 eV resolution and 100 eV pass energy, while the narrow scans (core levels) were taken with 0.2 eV resolution and 16 eV pass energy. The experiments were performed at a base pressure of 1×10^{-9} torr. Peaks were assigned from literature values: 285 eV for carbon, 533 eV for oxygen, 400 eV for nitrogen, 169 eV for sulfur, and 689 eV for fluorine [23]. The heights of the peaks were measured from the baseline and the ratio of the peak heights was taken as the relative abundance of the atoms on the sample surface. When comparing signals from different spectra, the peak heights were multiplied by appropriate scale factors.

Results and discussion

Microscopic study

Figures 1a and 1b represent the SEM micrographs of colloidal aggregate of S-PANI (freshly prepared) and the corresponding network (45 days after preparation), respectively. We describe the system of Fig. 1a as colloidal aggregate rather than colloidal crystal because of the lack of three-dimensional regularity. The formation of colloidal aggregate of S-PANI was explained to occur through a delicate balance of electrostatic forces

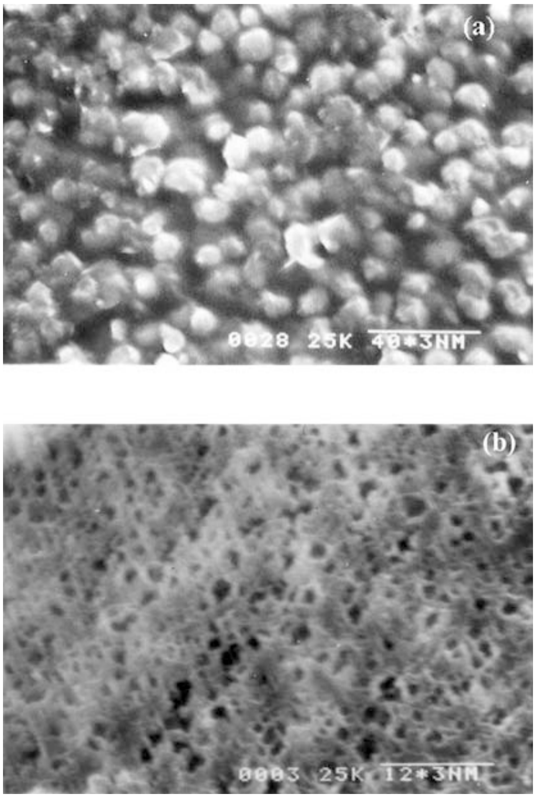


Fig. 1a, b SEM micrographs of **a** freshly prepared colloidal aggregate of S-PANI and **b** after aging for 45 days

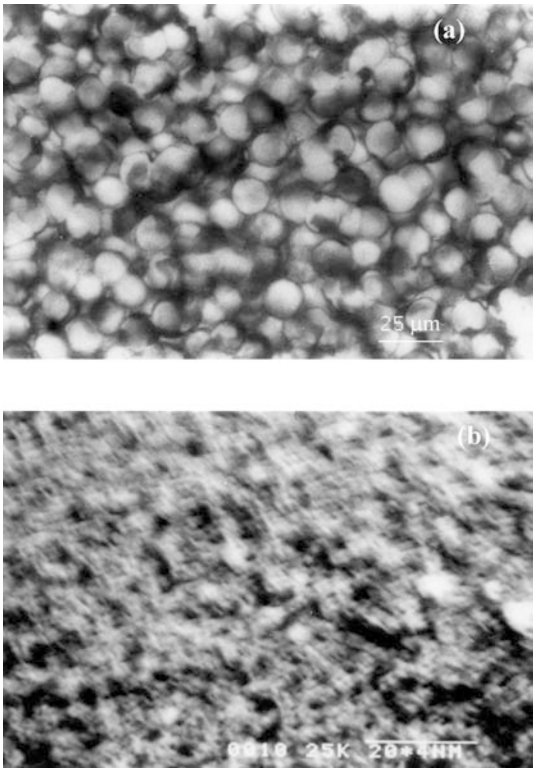


Fig. 2 **a** Optical micrograph of freshly prepared colloidal aggregate and **b** SEM micrograph after 90 days of aging of PVF_2–DBSA system

Table 1 Characteristics of the samples used in the work

Sample ID	Description	Morphology
Sample 1	S-PANI Na salt	Colloidal aggregate
Sample 2	S-PANI Na salt	Polymer network
Sample 3	PVF_2–DBSA	Colloidal aggregate
Sample 4	PVF_2–DBSA	Polymer network

between the latex particles and the vesicle surface [17]. In Figs. 2a and 2b the colloidal aggregate of the PVF_2–DBSA system and the corresponding network formed after 90 days are presented. The mechanism of formation of the colloidal aggregate from the PVF_2–DBSA system is not yet understood clearly. However, it is noteworthy that the surfactant-mediated colloidal aggregates produced either on vesicle surfaces or on solid glass surfaces were not stable even under desiccated conditions. These results indicate that the surfactant-mediated colloidal aggregates were metastable and they converted into a three-dimensional network structure on long-term aging. It was also observed that three-dimensional order of the colloidal aggregates was partially maintained in the net (Figs. 1b and 2b). The characteristics of the samples are summarized in Table 1.

Model for the colloidal crystal to net formation

A model for the colloidal crystal is shown in Fig. 3 where the polymer is situated at the core and the surfactant molecules remain on the surface (the shell). The surfactant molecules have long hydrocarbon tails, which sterically stabilize the latex particles from coalescence in the lattices. In colloidal aggregates the environment is different from that in the lattices. Here the colloidal particles are orderly placed in their own medium and they are more closely packed. So there is a chance of interdigitation of the surfactant tails, and some interdigitation might occur during the colloidal crystal formation. On aging, the interdigitation of the surfactant tails proceeds further if the room temperature (T) is above the glass transition temperature (T_g) of the aggregate. So there may exist a rate process of interdigitation of surfactant tails and it would depend on ($T-T_g$): the larger the difference, the faster will be the rate of interdigitation. In the present work we could not observe any T_g down to −30 °C for both the systems in our DSC instrument, so ($T-T_g$) is greater than 60 °C, allowing the interdigitation process. The force behind the interdigitation is the cohesive force of attraction of the surfactant tails. Due to this interdigitation process

Fig. 3 A model for the conversion of polymer colloidal crystal into network on aging

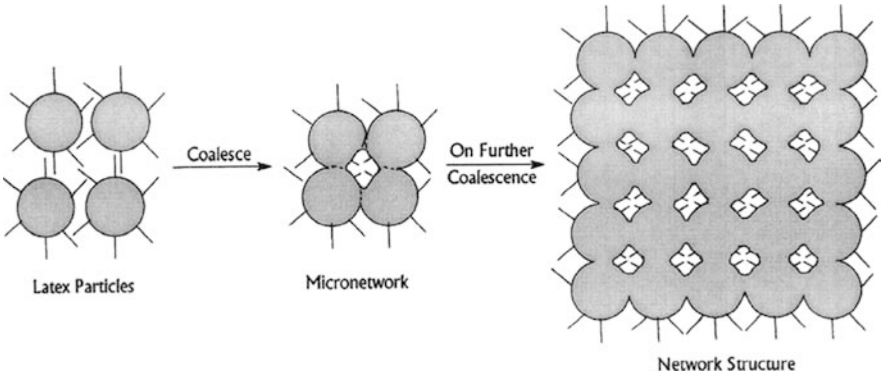
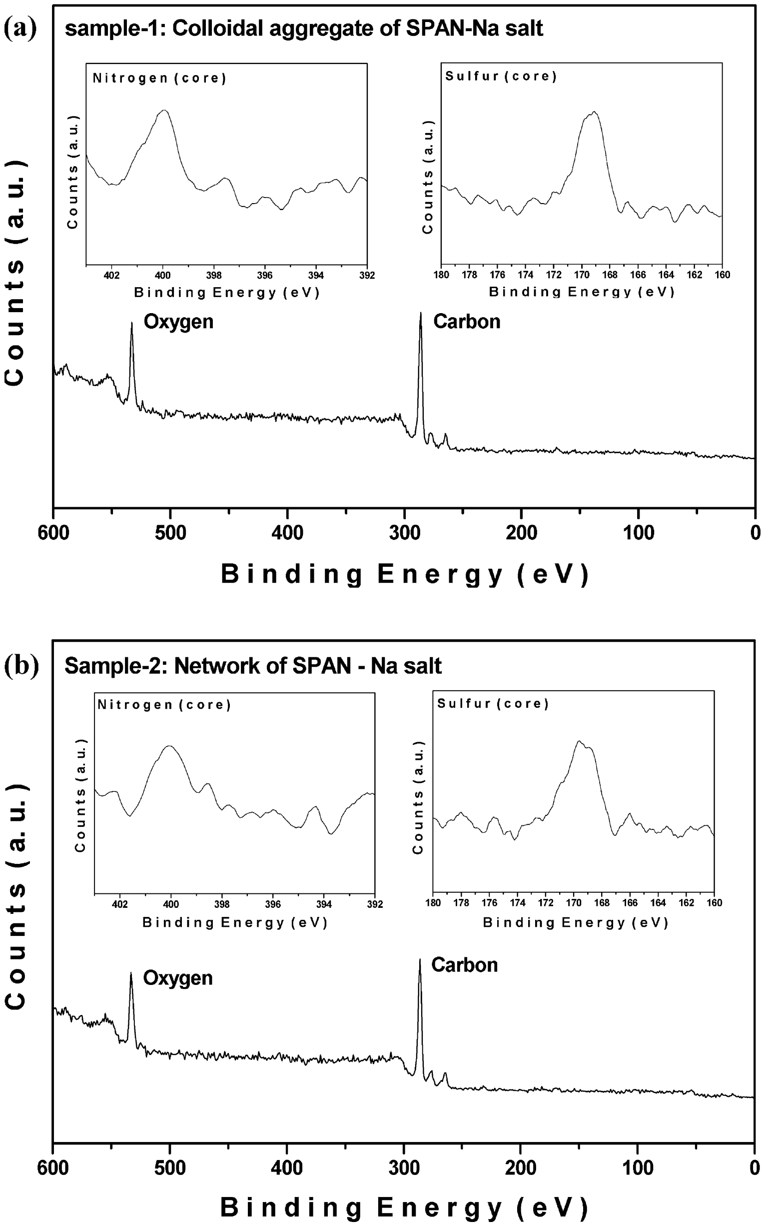


Fig. 4a, b X-ray photoelectron spectra of **a** colloidal aggregate of S-PANI and **b** corresponding network formed after 45 days of aging; *inset*: core-level spectra (see text)



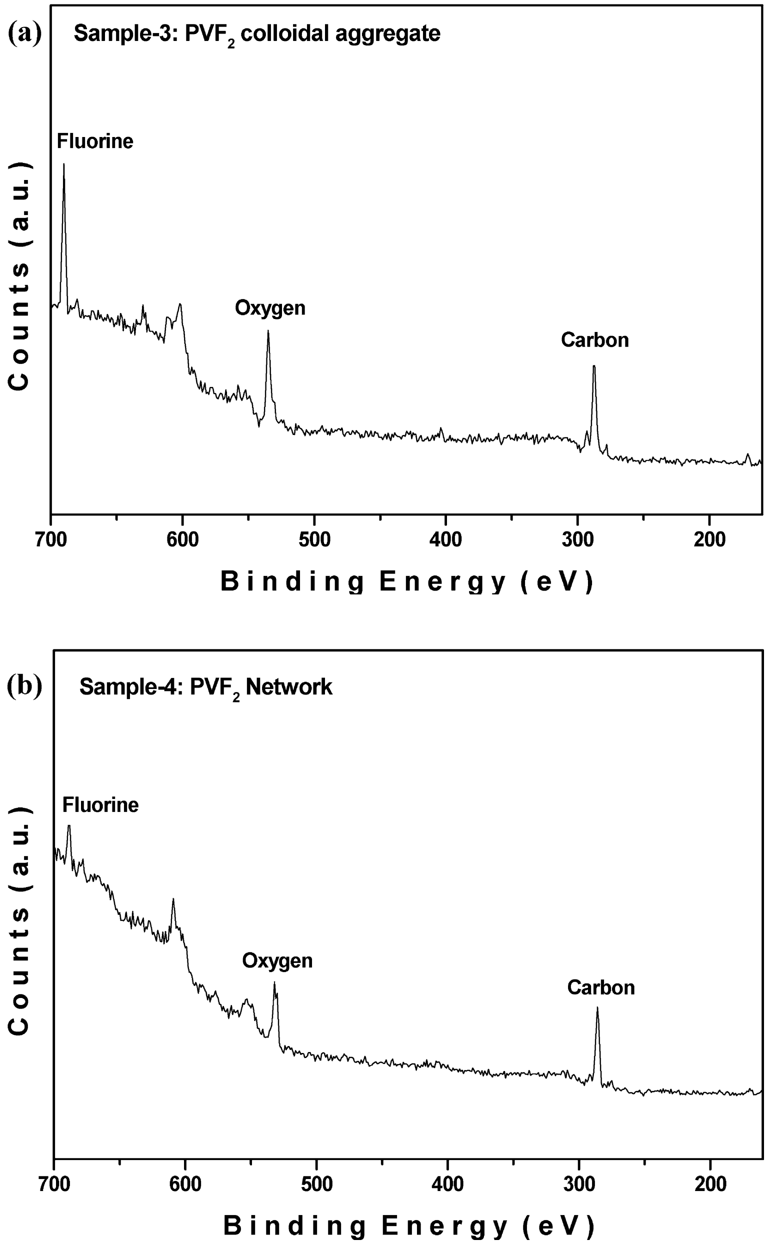


Fig. 5a, b X-ray photoelectron spectra of **a** colloidal aggregate of PVF$_2$–DBSA system and **b** corresponding network after 90 days of aging. The peaks around 590 to 635 eV are from X-ray source

coalescence of the colloidal aggregates occurs as shown in Fig. 3 and it proceeds with time to produce the network structures. Therefore, the interdigitation process destabilizes the colloidal aggregates and it gradually transforms them into a net. A proof for this model is presented from the elemental content analysis of the surface using X-ray photoelectron spectroscopy (XPS).

XPS study

The X-ray photoelectron spectra of colloidal aggregates and the corresponding net samples of S-PANI and PVF$_2$–DBSA systems are presented in Figs. 4 and 5, respectively. In the S-PANI system the peaks of oxygen (O) and carbon (C) atoms appear at 535 and 285 eV, respectively. The two small peaks near 285 eV might arise due to aromatic C atoms [23]. The peaks for nitrogen (N) and sulfur (S) atoms are not prominent in the spectra. To determine the concentrations of N and S, core-level analysis at 400 and 169 eV was performed and they are shown in the insets of Figs. 4a and 4b. The relative abundance of different atoms on the surface, calculated from the ratio of the peak heights of the respective atoms, is presented in Table 2. For the colloidal aggregate and network of the PVF$_2$–DBSA system (Figs. 5a and 5b), the relative abundances of the elements C, O, and F were calculated from the peak-height ratio in

Table 2 Concentration ratio of various atoms at the surface of polymer colloidal aggregates and at the corresponding polymer networks of S-PANI and PVF_2–DBSA system obtained from XPS analysis

Sample	Concentration ratio	Colloidal aggregate	Polymer network
S-PANI	C/N	22.8	43.7
	C/S	22.1	38.3
	S/N	1.0	1.1
	C/O	1.5	1.7
PVF_2–DBSA	C/F	0.6	2.3
	C/O	0.9	1.2
	F/O	1.5	0.5
	C/S	13.4	12.4

the same wide-scan spectra while that of S was determined from the core-level analysis. These results are also summarized in Table 2.

In colloidal aggregates, XPS can detect the C atoms of the surfactant at the surface as well as a larger part of the N atoms from the core S-PANI through the vacant space at the surface. But in the network the surfactant tails interdigitate, decreasing the vacant space and making the core N of S-PANI less available. Consequently, both C/N and C/S ratios should be higher in the polymer network than those in the colloidal aggregate. In the S-PANI system both C/N and C/S values in the polymer network were almost double those in the corresponding colloidal crystal (Table 2). The S/N ratio remained almost the same both in the colloidal crystal and in the net because SO_3H groups are anchored from the N atoms of PANI making the S/N ratio independent of morphology. The C/O ratio increased about 14% in the network relative to that of the colloidal crystal of S-PANI. The oxygen is within the SO_3H group of the surfactant, therefore a small increase in the C/O ratio is probable after the conversion of colloidal crystals into network. Compared to C/N or C/S this increase is less because the oxygen is located at a less interior position than the location of nitrogen and sulfur.

In the PVF_2–DBSA system the C/F ratio was about four times larger in the network than that in the colloidal aggregate (Table 2). The surfactant tails, which stabilize the colloidal form of PVF_2 in the solvent, begin to interdigitate during formation of colloidal aggregate. Interdigitation increases with aging time of the colloidal aggregate and it forms the network structure .As a result the net surface possesses less vacant space than that of colloidal aggregate. Consequently, the C/F ratio in the polymer net increases to such a large extent because core F atoms are then less available for XPS than in the colloidal aggregate. The C/O ratio increases by 30% in the network and this is similar to that of the S-PANI system. The decrease in F/O ratio in the network indicates that the interdigitated surfactant tails in the network shield the F atoms of PVF_2 more than the O atoms of the surfactant. This is probable, as F atoms which anchor the $-SO_3H$ group remain in a more interior position than the O atom. The almost same C/S ratio in the colloidal aggregate and in the network indicates that S is situated at the same position both in the colloidal crystal and in the polymer network.

Conclusion

The surfactant-mediated colloidal crystal-like aggregates of S-PANI and PVF_2 are metastable and convert into polymer networks on long-term aging even in desiccated conditions. A model considering the interdigitation of the surfactant tails and subsequent coalescence of the colloidal particles with time has been proposed for this conversion. XPS study reveals that the relative abundance of carbon atoms on the surface of the polymer network is highly increased compared with that of the colloidal aggregate. This observation supports the proposed model for the conversion of colloidal aggregate into polymer network.

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