CHEMISTRY LETTERS, pp. 209 - 212, 1984.

CRYSTALLIZATION OF POLY(ETHYLENE GLYCOL) DI-9-ANTHROATE ADSORBED ON POLY(METHACRYLIC ACID) MEMBRANE IN WATER[1]

Yoshihito OSADA* and Masayoshi KOIKE

Department of Chemistry, Ibaraki University, Mito 310

A poly(ethylene glycol) di-9-anthroate made adsorption on the poly(methacrylic acid) membrane through polymer membrane complexation in water and crystallized spontaneously to give a single-crystal with unique morphological texture on the surface of the membrane.

We reported previously that the mechanochemical system consisting of a crosslinked poly(methacrylic acid)(PMAA) membrane and the solvated poly(ethylene glycol)(PEG) can isothermally develop contractile forces under isometric condition.[2,3] The energy conversion from chemical into mechanical of this type was based on the macromolecular association between solvated PEG and PMAA membrane through cooperative hydrogen bonding giving rise to conformational changes of the membrane network.[4,5] In this communication we report that poly(ethylene glycol) di-9-anthroate(PEG-ant; molecular weight of PEG: 3000) forms polymer - membrane complex with PMAA and undergoes spontaneous self-organization having higher-ordered structure.

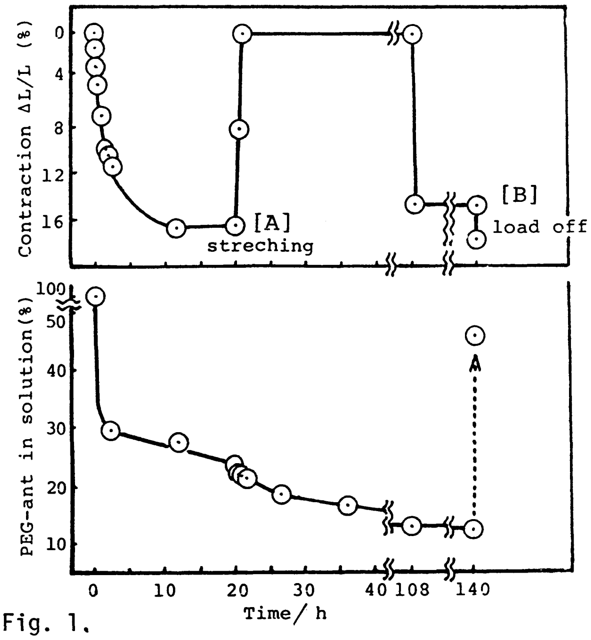


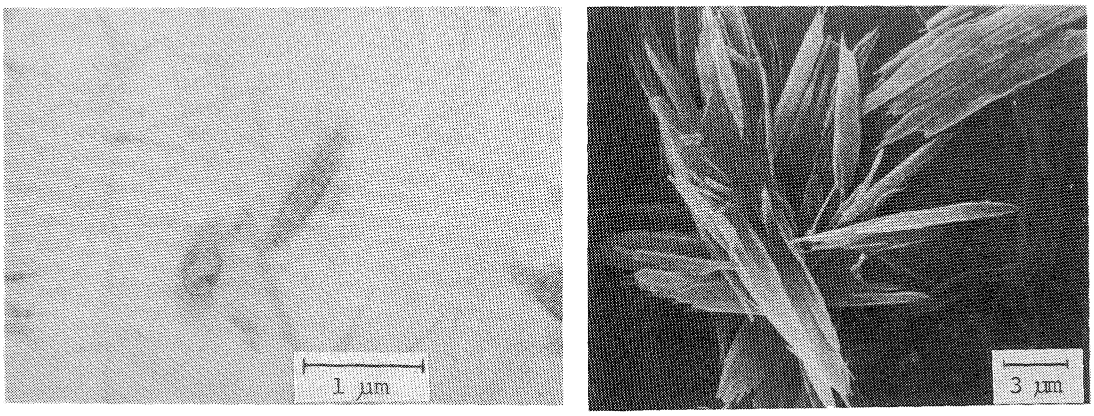
Fig. 1.
Profiles of contraction of PMAA membrane and concentration change of PEG-ant.
PMAA membrane: 65 mm x 10 mm x 28 μm, 14.4 mg(dry) weight, load: 500 mg, PEG-ant: 12 mM(per repeating unit of PEG), Temp: 25 °C

Figure 1 shows the profiles of isothermal contraction of the PMAA membrane observed on addition of PEG-ant and its change in concentration measured at the same time. It is seen that the addition of PEG-ant produced a effective contraction of the membrane which tends to saturate after ca. 10 h. The decrease in PEG-ant concentration in embedding solution indicates that the effective adsorption of PEG-ant to the membrane occurred in parallel to the contraction. A stretching of the membrane by increasing load [A] in order to recover the initial length of the membrane caused an additional adsorption of PEG-ant, the value of which attained nearly 90% of total PEG-ant.

On the contrary, a shrinking of the membrane by removing the load[B] resulted in a desorption of PEG-ant from the membrane, and the amount of the PEG-ant adsorbed decreased from 90 to 50%(reverse-mechanochemical reaction). Thus, it is clear that the adsorption-desorption equilibrium of PEG-ant on the PMAA membrane can be closely associated with the mechanical conditions of the membrane, and indicates the possibility to control the chemical equilibrium by applying a mechanical energy to the system. Similar adsorption-desorption relation was also observed under isometric condition; adsorption of 62% of total PEG-ant developed 1.85 kg/cm^2 of stress and the complete relaxation of the membrane released the 70% of PEG-ant adsorbed.

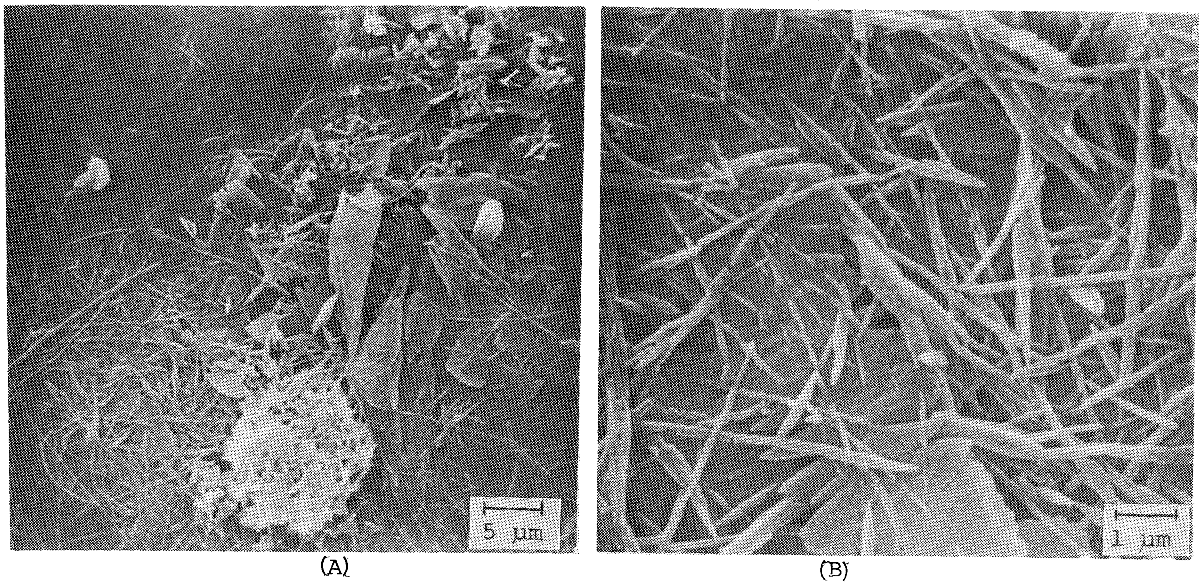
Interesting feature was observed when the PMAA membrane embedded in the PEG-ant solution was allowed standing at constant temperature. It was found that the PEG-ant adsorbed to the membrane spontaneously crystallized at the surface of the membrane to give a single crystal with interesting morphology.

The microcrystals with needle-like shape 0.5 - 1.0 µm long(Fig. 2A)were initially observed under optical microscope with crossed nicols and by scanning electron microscope, which tended to aggregate each other in a few hours by immersing membrane in the PEG-ant solution(Fig. 2B). The crystal growth was rather rapid and after 5-10 h of aging time massive crystal-aggregates were formed as shown in Figs. 3A and 3B. A number of needle-like crystals formed in the initial stages seem to gather side by side into a bigger plate-like crystal or combine head to head into a sort of fibrous structure. Increasing concentration of PEG-ant and aging time at constant temperature apparently took the PEG-ant solution into conditions favoring more dense aggregate growth and more rapid growth.



(A) (B)

Fig. 2. Scanning electron micrograph of PEG-ant crystals formed in the initial stages.
aging time: (a) 3 h; (b) 5 h, room temp.
PEG-ant: 12 mM, PMAA membrane: 10 mm x 10 mm x 20 µm.



(A) (B)

Fig. 3. Scanning electron micrograph of PEG-ant crystals formed in the later stages. aging time: 7.5 h, room temp , PEG-ant: 75 mM, PMAA membrane: 10 mm x 10 mm x 20 μm. Note the formation of plate-like and fiber-like crystals.

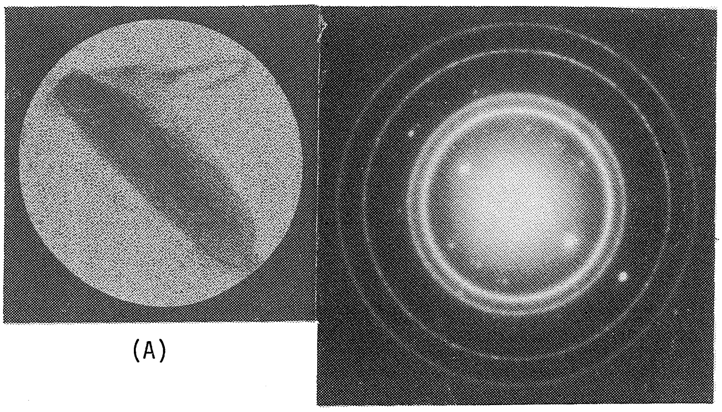
The complex formation between PEG-ant and PMAA on the surface of the membrane plays an essential role for the crystallization, particularly for the nucleation process, since PMAA membrane is the only membrane at present that can adsorb PEG-ant from the solution and can build up the crystallites. No crystal growth and PEG-ant adsorption was observed on the membranes of poly(acrylic acid)(PAA), poly(ethylene) or poly(ethylene terephthalate).

We have previously reported that the polymer complex between PEG and PMAA was much stable than that formed from PEG and PAA(stability constants of PEG-PMAA and PEG-PAA are 250 and 9 l/mol, respectively at 30 °C 6)). It was also found that the fluorescence intensity of PEG-ant increased more than 10 times by addition of PMAA due to the complex formation in water.7) In contrast with this, no fluorescence increase was observed by addition of PAA . Since an increase in fluorescence intensity could be associated with rather tight "binding" or "fixing" of anthracene chromophores in the hydrophobic domain of the complexes, the cooperative complexation of the macromolecular chains is adequately considered to promote the nucleation of the crystal growth.

It should be noted that PEG(having no anthracene groups) could adsorb on the PMAA membrane and form the complex-aggregates.8) However, they were of undefined shape and size with no higher-ordered structure and were quite different from those obtained by PEG-ant. Thus, the strong inter-macromolecular hydrogen bonding between PEG chains and steric stacking considerations between anthracene groups seem to have made this interesting crystalline organization.

In order to investigate the molecular orientation and structure in the plate-like crystals formed in the later stages of the organization, a selected-area electron diffraction study was made using a microcrystal 1.7 μm long and 0.5 μm wide(Figs. 4A and 4B; Hitachi model HU-11C electron microscope was used).

Sharp spots clearly indicate that the microcrystal is of single-crystal (rings are due to evaporated gold by which a camera length was calculated). Needle-like crystal smaller than 0.1 μm wide formed in the earlier stage also showed the similar diffraction pattern although the intensity was weaker. Lattice distances of the single-crystal was calculated using (100) and (010) (table 1). The diffraction which corresponded to the reflections from ((hk0)) planes of the unit cell shows that the molecular chains are aligned perpendicular to the surface of the crystallite. From these results it was concluded that the PEG-ant single-crystal grown on the surface of PMAA membrane has a unit cell of orthorhombic system with spacings a=0.6732 nm and b = 0.6177 nm. These values are different from the unit cells of PEG with monoclinic (a=0.805, b=1.304 nm)[9] or triclinic (a=0.471, b=0.444 nm)[10] system and of anthracene (a=0.856, b=0.604 nm)[11] with monoclinic system.


(A)

(B)

Fig. 4.
Electron diffraction pattern(B) obtained from the crystal of PEG-ant(A).

Table 1. Lattice distances of single crystal of PEG-ant.

(h k l)	θ	Lattice Distance(nm)	
		(obsd)	(calcd)
(1 0 0)	-	-	0.6732
(2 0 0)	0.3736	0.3366	0.3366
(3 0 0)	-	-	
(4 0 0)	0.7470	0.1684	0.1683
(5 0 0)	-	-	
(6 0 0)	1.1202	0.11228	0.1122
(0 1 0)	(0.2036)	0.6177	0.6177
(1 1 0)	-	-	
(2 1 0)	0.4311	0.2918	0.2956
(3 1 0)	-	-	
(4 1 0)	-	-	
(0 2 0)	0.4071	0.3089	0.3089
(1 2 0)	0.4466	0.2816	0.2807
(2 2 0)	-	-	
(3 2 0)	0.6920	0.1817	0.1815
(4 2 0)	-	-	
(0 3 0)	0.5986	0.2101	0.2059
(1 3 0)	-	-	
(2 3 0)	0.7016	0.1793	0.1756
(3 3 0)	-	-	
(0 4 0)	0.7901	0.1592	0.1544
(1 4 0)	-	-	

The authors are grateful to Mr. T. Yamamoto and Y. Kondo(Kanebō Co. LTD) for taking electron diffraction diagrams and useful discussion. Support by the Grant-in Aid from the Ministry of Education, Science, and Culture, Japan, No. 56550619, is gratefully acknowledged.

References

1) Study of Mechanochemical Reaction.XV, Part XIV: Nippon Kagaku Kaishi, 1983, 812.
2) Y. Osada and M. Sato, Polymer, 21, 1057(1980).
3) Y. Osada, J. Polym. Sci., Polym. Chem. Ed., 15, 255(1977).
4) Y. Osada and Y. Takeuchi, J. Polym. Sci., Polym. Lett. Ed.,19,303(1981);Polym.J.,15,279(1983).
5) V. A. Kabanov, IUPAC Macromol. Chem., 8, 121(1973).
6) Y. Osada, J. Polym. Sci., Polym. Chem. Ed., 17, 3485(1979).
The principle and the method of mechanochemical reaction presented here are essentially the same as described in 2) and 3). The mechanism of the complexation and the application of mechanochemical system are described in 5), 6), and 4), respectively.
7) Y. Osada, M. Koike, and E. Katsumura, Chem. Lett., 1981, 809.
8) Y. Osada, J. Polym. Sci., Polym. Lett. Ed., 18, 281(1980).
9) Y. Takahashi and H. Tadokoro, Macromolecules, 6, 672(1973).
10) Y. Takahashi and H. Tadokoro, J. Polym. Sci., Polym. Phys. Ed., 11, 2113(1973).
11) Kagaku Benran(Handbook of chemistry),2nd ed, Fundamental Ed. II,Chemical Society of Japan, p.1447.

(Received November 7, 1983)