

PREPARATION OF PERFLUOROOCTANOYL-MODIFIED POLY(VINYL-ALCOHOL)S AND THEIR ADSORPTION AT AN AIR-WATER INTERFACE*

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Abstract Perfluorooctanoyl modified poly(vinyl alcohol)s (FPVA) were prepared by means of substituting a small amount of hydroxyl groups on the backbone of poly(vinyl alcohol), for which the initial degree of polymerization is equal to 1750. The substitution extent, defined by the number of substituting units in a chain, for the four FPVA samples was in the range of 0.5–5 perfluorooctanoyl groups per chain. The FPVA samples with the highest substitution extent still had good solubility in water. It was shown by experimental measurement at $30.0 \pm 0.1^\circ\text{C}$ that the surface tension of the aqueous solution of the highest substituted FPVA decreased to 16.6 mN/m at a higher concentration, *e.g.* about 0.1 g/mL. Obviously, macromolecules of FPVA exhibit a very strong tendency to adsorb at the air-water interface, because the hydrophobic perfluorooctanoyl groups in FPVA have a very high surface activity as they are in small molecular fluorinated surfactants. The chain conformation of such a model polymer adsorbed on the air-water interface was also discussed.

Keywords Modified poly(vinyl alcohol), Perfluorooctanoic acid, Surface tension, Macromolecule surfactant, Adsorption, Chain conformation, Air-water interface

INTRODUCTION

Macromolecular surfactants have attracted many chemists interested in surface activity together with polymeric properties not only for scientific reasons, but also because of their potential special applications^[1–4]. Some reports appeared recently on the syntheses and characterization of modified water-soluble polymers [such as polyethylene glycol and poly(*N*-isopropylacrylamide)] with perfluoroalkyl groups^[5–9]. Poly(vinyl alcohol) (PVA) is well known as a widely used hydrophilic polymer and it is soluble in water because of the large number of hydroxyl groups present as side groups on the backbone. In principle, the hydrophilicity of PVA may be varied by the reaction of hydroxyl groups with hydrophobic substances. As a result the product may have some new features, especially surface activity. In the present work we have attempted to substitute a small amount of the hydroxyl groups on PVA chains with the average degree of polymerization 1750 by perfluorooctanoyl groups in order to prepare a series of surface-active perfluorooctanoyl modified poly(vinyl alcohol)s (FPVAs). The substitution extent of perfluorooctanoyl groups for four samples used in experiments was in the range of 0.5–5 groups per chain. The measurement of the surface tension of the aqueous solution was carried out by the drop-volume method for these FPVA samples. The FPVA sample with the highest substitution extent is still well soluble in water, the surface tension of which in aqueous solution decrease to 16.6 mN/m at a higher concentration, *e.g.* about 0.1 g/mL, at $30.0^\circ\text{C} \pm 0.1^\circ\text{C}$. At the end of this paper, we suggest possible models for the adsorption of FPVA at the air-water interface and deduce a thermodynamic equation for an adsorbed chain with the middle segment at the air-water interface. It was found that its available conformational number relating

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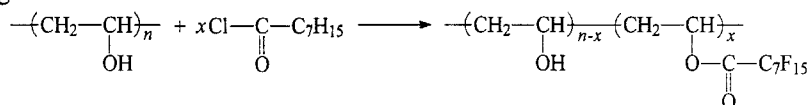
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to the adsorption entropy is at least less than that of the tail chain by a factor $N^{-1/2}$, where N is the degree of polymerization, *i.e.* the chain length, for the model chain.

EXPERIMENTAL

Synthesis of Perfluorooctanoyl Modified Poly(vinyl alcohol) (FPVA)

Preparation of the perfluorooctanoyl-substituted poly(vinyl alcohol) was carried out by a typical esterification reaction following this scheme:



The esterification was performed at 150°C in *N,N*-dimethyl formamide (DMF). The PVA selected for this experiment was purchased from Beijing Baili Chemical Development Center (BLQ1028-96). Its DP is 1750. The bound water in PVA was eliminated by azeotropic distillation with methylbenzene before the esterification. Perfluorooctanoyl chloride was obtained by the acylation reaction between the corresponding acid and sulfinyl chloride with pyridine as the catalyst^[10]:



The synthesis procedure of FPVAs, for example, sample 3, is described as follows. PVA (1.0 g) was dissolved in 40 mL DMF in a three-necked flask at 150°C with stirring under nitrogen. After the solution became transparent, the temperature was lowered to 100°C. About 0.5 mL pyridine was put into the flask as a catalyst, then perfluorooctanoyl chloride was slowly added. The reaction maintained for 10 h at 100°C. The resulting product was precipitated by methanol, washed with hot benzene to remove the solvent and unreacted perfluorooctanoyl chloride. The product (FPVA) was dried in a vacuum drier, then weighed. It is easy to calculate the product yield.

Analysis with Ion Exchange Chromatography

The substitution extent of all samples was determined by ion exchange chromatography, using a Dionex 4500i. With a chromatographic column A54A-SC under the condition of 85% humidity at 26°C, the procedure followed general analysis method (JY/T 020-1996). A definite amount of a sample was combusted in oxygen and then the gas released from the process was adsorbed by 40 mL 20 mM $\text{Na}_2\text{B}_4\text{O}_7$ that was dissolved in de-ionized water. In the process, the efflux was 2.0 mL/min and 10 μs CDM detector was needed. According to F-ion content data from the measurement, the substitution extent, *i.e.* the number of substituting units in a chain, for FPVA samples was calculated.

Measurement of Surface Tension

The drop-volume technique was employed in the same way as reported in Ref. [5].

RESULTS AND DISCUSSION

Substitution Extent for FPVAs

The F-ion content (wt%) in the samples was determined quantitatively by ion exchange chromatography. The extents of substitution on one PVA chain by perfluorooctanoyl groups are listed in Table 1. The results indicate that the extent of substitution of perfluorooctanoyl groups on the backbone of PVA, *i.e.* the number of perfluorooctanoyl groups per chain, increases with increasing molar ratio of perfluorooctanoyl chloride to poly(vinyl alcohol).

Surface Tension of Aqueous Solution of FPVAs

The surface tensions of perfluorooctanoic acid, PVA and FPVAs (four samples) as a function of bulk concentration at $30.0^\circ\text{C} \pm 0.1^\circ\text{C}$ (Fig. 1) were determined and a comparison of their values demonstrated that perfluorooctanoyl groups could affect the surface tension greatly. The values of surface tension of FPVAs

decreased with the increase of the molecular number of perfluorooctanoyl groups per chain or the concentration of the polymer solution. Obviously, the perfluorooctanoyl group tends towards the air-water interface due to its strong hydrophobicity. As a result, the polymer chain in the solution was forced to move to the surface.

Table 1. The yield and perfluorooctanoyl substitution extent of FPVAs

Sample no.	PVA (g)	Perfluorooctanoyl chloride (g)	Molar ratio ^a	FPVA yield (wt%) ^b	F-ions content (wt%)	Substitution extent ^c
1	2.00	1.30	0.0902	60.8	0.190	0.51
2	2.00	1.95	0.135	51.1	0.630	1.72
3	1.00	1.40	0.194	42.2	1.00	2.75
4	1.00	2.00	0.277	34.2	1.82	5.04

^a The molar ratio of perfluorooctanoyl chloride to the unit of PVA
^b The weight percentage of FPVA based on the weights of PVA and perfluorooctanoyl chloride
^c The molar number of perfluorooctanoyl group contained in one FPVA chain

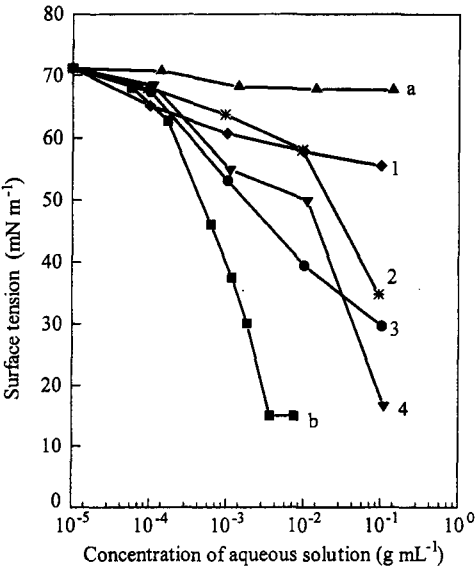


Fig. 1 Surface tensions of aqueous solutions of PVA (a), perfluorooctanoic acid (b) and FPVAs with different substitution extents as listed in Table 1 (sample 1, 2, 3, 4)

Molecular Area of FPVAs at Air-Water Interface

From Gibbs adsorption theory^[11] we know

$$\Gamma = \frac{1}{RT} \frac{\partial \gamma}{\partial \ln c} \tag{1}$$

where Γ is the amount of adsorbed surfactant per unit area, R the gas constant, T the absolute temperature, γ the surface tension and c the bulk concentration of the surfactant solution. Thus, we could obtain the molar number of adsorbed molecules per unit area of the surface from the semi-log arithmetic plot relating the surface tension γ to the concentration c . Then, it is easy to calculate the area a_0 per surfactant molecule at the air-water interface using the following expression:

$$a_0 = \frac{1}{N_{av} \Gamma} \tag{2}$$

where $N_{av} = 6.022 \times 10^{23}$, i.e. Avogadro's number. The values of a_0 obtained by the previous method for the determination of the surface tension are listed in Table 2.

It is known from Tables 1 and 2 that the sample 1 of FPVA has the lowest substitution extent. In other words, its number of perfluorooctanoyl groups per FPVA chain is much lower than that of the other samples. In fact the sample of such a FPVA could be regarded as a mixture of pure PVA and FPVA with a small substitution extent. So, the discussion of the surface behavior is less interesting. We now turn to a discussion about the behavior of FPVA with a higher value of substitution extent, *e.g.* sample 4. As seen from Table 1, the substitution extent of this FPVA sample is 5.04. It means that each chain contains approximately five perfluorooctanoyl groups. In consideration of the statistics of polymer reaction, it should be noted that the number of substituting groups in each polymer chain is not homogeneous at all. However, ignoring the real distribution of the substitution extent in detail, we simply consider that each chain of sample 4 contains five perfluorooctanoyl groups as a statistical average.

Table 2. Surface concentration Γ and molecular area a_0 for aqueous solution of perfluoroheptyl end-capped poly(vinyl alcohol) of samples 1 to 4, ordinary poly(vinyl alcohol) (a) and perfluorooctanoic acid (b)

Sample	A	1	2	3	4	b
$-\partial\gamma/\partial\ln c$ (mN/m)	0.416	1.68	3.61	5.50	8.31	17.24
$\Gamma \times 10^{11}$ (mol/cm ²)	1.65	6.67	14.32	21.82	32.96	68.40
a_0 (nm)	10.06	2.49	1.16	0.76	0.50	0.24

It is interesting to note that the best surfactants with low molecular weights at or above critical micelle concentration could decrease the surface tension of their aqueous solutions to 12–15 mN/m^[11]. Sample 4 with the highest substitution extent was more interesting because its surface tension of aqueous solution decreases to 16.6 mN/m (Fig. 1) at about 0.1 g/mL, suggesting that almost all of the perfluoroalkyl groups were disperse on the surface. It was noted that, in the same situation, the concentration of FPVA was much higher than that of PEO end-capped with perfluoroalkyl groups (only about 0.01 g/mL)^[5].

Molecular Conformation for Adsorbed Polymer Chain

As far as the detailed structure is concerned, two extreme conformations could be constructed as shown in Fig. 2. First, let us look at one of these extreme situations shown at the left of the Figure, *i.e.* the macromolecular chains contain perfluorooctanoyl groups on their middle position of the backbones. This adsorbed chain forms two shorter tail chains, when it is adsorbed on the surface (Fig. 2a). It was known from the previous theory^[12–14] that a long tail chain with N as the degree of polymerization, in the process of its formation, will decrease the conformational number by $N^{1/2}$ in comparison with a free chain having the same length. In more detail, when one end of the chain is adsorbed at the surface according to the definition of a tail chain, the ratio $\alpha_1(N)$ of the conformational number for a tail to that for the free polymer chain is

$$\alpha_1(N) \approx \frac{1}{\sqrt{6\pi}} N^{-1/2} \quad (3)$$

$$\sim N^{-1/2}$$

If the adsorbed chain was constructed in accordance with the model shown in Fig. 2(a), it could be thought of as two short tails. One of the two tails has the length x , the other $(N - x)$. Based on the previous equation and the basic principles of statistics, the ratio α_m of the conformational number for such a chain to that for the free chain is given in the approach to the infinite length:

$$\alpha_m(N) \approx \frac{1}{N} \int_0^N \frac{1}{6\pi} [x(N-x)]^{-1/2} dx$$

$$= \frac{1}{6\pi N} \arcsin \left(\frac{2x-N}{N} \right) \Big|_0^N \quad (4)$$

$$\sim N^{-1}$$

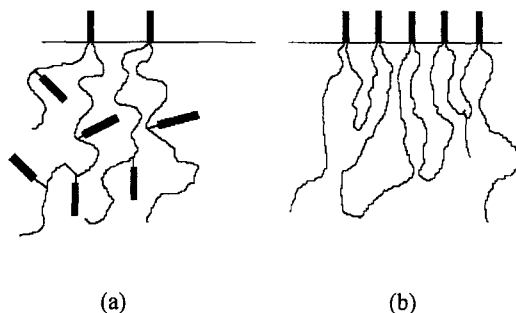


Fig. 2 Two extreme conformations of FPVA molecules with a high substitution extent when they are adsorbed on the air-water interface

Note the obvious difference in the power between Eqs. (3) and (4). The above calculation means that the entropy factor is unfavorable for the adsorbed chain with the middle segment at the surface in comparison with the tail chain. If the adsorbed group is identical the free energy for the adsorbed chain modeling in Fig. 2(a) is less favorable than that for the tail chain^[12, 13]. In other words, the location of the adsorbed group in the chain is important for its adsorption entropy. In comparison with the tail chain, the adsorbed chain with the middle segment will decrease its adsorption entropy by $N^{1/2}$, which is very large when $N \gg 1$. Maybe this is the reason why the surface activity of the FPVA reported here is weaker than that of other polymers end-capped by perfluorinated groups reported previously^[5, 7].

Then we go further to the discussion of the other extreme situation explained in Fig. 2(b). In this case, the entropy factor is more unfavorable than that for the free chain. Besides two short tails, there are many small loops in such an adsorbed chain. A theory^[14, 15] also tells us that the loop chain has a lower thermodynamical probability than a free or tail chain. However, the energy factor of the adsorbed groups also plays an important role in the adsorption. If the energy factor is dominant, this extreme conformation expressed in Fig. 2(b) will happen. Up to now it has been very hard to discuss quantitatively the energy and entropy factors for the adsorbed chain in detail. The complete analysis of thermodynamics for this particular case of polymer adsorption will be considered in future studies.

From our experimental results about the molecular area a_0 for perfluorooctanoyl-modified PVA with the highest substitution extent (5.04) (*i.e.* sample 4), it was suggested that its value of a_0 is equal to 0.503 nm^2 , which is almost twice as much as the molecular area of a perfluorinated group. In other words, this means that about two perfluoroalkyl groups in each chain are adsorbed in the meaning of a statistical average. Therefore, the practical situation of FPVA with the high substitution extent lies between the extreme ones in Fig. 2(a) and (b).

The adsorption phenomenon of a polymer system is very complicated indeed. In addition to the thermodynamics, the dynamic factor will sometimes be dominant. For example, from the viewpoint of the dynamics, the diffusion of the polymer chain to the surface was a very difficult motion in relation to the so-called "hair needle" motion^[16].

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