

Existence of Critical Aggregation Concentration at the Very Dilute Regime of Poly(vinylidene fluoride)/Propylene Carbonate System

Il Hyun Park,^{*} Zhi Yang Xu, Yun Ling, Bong Soo Kim,^{*} and Jang Oo Lee[†]

Department of Polymer Science and Engineering, Kumoh National Institute of Technology, Gumi, Kyungbuk 730-701, Korea

^{*}E-mail: ilhyun@kumoh.ac.kr

[†]Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

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Since poly(vinylidene fluoride) (PVDF) has been known as a typical semicrystalline polymer with strong piezoelectric and pyroelectric properties, lots of scientific researches have been focused on these topics. In addition, recently, thermoreversible physical gelation¹⁻⁸ is regarded as another interesting field of PVDF on the ground of the reports of Cho,⁹ Nandi,¹⁰⁻¹⁴ and Park.¹⁵⁻¹⁷ Especially, Cho *et al.* have found first that PVDF/ γ -butyrolactone(BL) system can form a transparent and thermoreversible gel.⁹ Next Nandi and his coworkers¹⁰⁻¹⁴ systematically have investigated this physical gelation phenomena of PVDF in a wide range of concentration and temperature in various solvents such as acetophenone, ethyl benzoate and glyceryl tributyrate. One of their observations is that physical gelation occurs even at very low polymer concentration like $C_{gel} \sim 1$ wt%. According to Park's observation,^{16,17} PVDF polymers even in pregel state do not exist as separated single chains but form aggregates of core-shell structure with the outer radius ~ 350 nm and very narrow size distribution.

When the dissolving process of PVDF powders in propylene carbonate solvent at ~ 170 °C are analyzed stepwise, first PVDF powders become transparent due to swelling and then a lot of thin hazes occur near the swollen transparent powders and at last all PVDF powders go out of our view within ~ 30 minutes. However it is observed by means of laser light scattering that PVDF structure in PC (or BL) solution of $C > 1 \times 10^{-4}$ g/mL has always kept as a core-shell form. For a reasonable explanation of this, first each PVDF chain on the outside surface of powder (or pellet) is dissolved as a separated single chain. Second as soon as PVDF concentration reaches some critical aggregation concentration (CAC), the PVDF chains aggregate and form core-shell structure.¹⁶⁻¹⁸ Therefore the main goal of this study is to find out experimentally whether this kind of critical concentration exists or not. And if it exists, what is the order of the CAC? To carry out this, at very wide concentration range ($5 \times 10^{-7} < C < 10^{-3}$ g/mL) of PVDF/PC system, the particle size has been investigated by the laser light scattering as a function of PVDF concentration.

Experimental section

PVDF used in this study was purchased from Aldrich

(Cat. No. 18270-2) and its nominal molecular weight was given as 534,000 g/mol. Propylene carbonate (PC; Aldrich Cat. No. 414220) was used as solvent of PVDF. As its refractive index $n_{25}^D = 1.4199$ was very close to that of PVDF ($n_{25}^D \sim 1.40$), the specific increment of refractive index of this system, dn/dC was measured as -0.012 mL/g at 514 nm and 40 °C. Although such a small value of dn/dC is surely undesirable condition due to weak scattered intensity, PC has been selected as our solvent because of several strong points such as (i) very good dissolving power for PVDF, (ii) no phase separation at room temperature contrary to other systems, (iii) convenience of comparison with our previous data. For light scattering experiment, optically clean (*i.e.* dust-free) PVDF mother solution of 3×10^{-3} g/mL was obtained by the centrifuging method (4000 rpm, 30 min at 25 °C). All kinds of dilute solution samples were prepared inside the dust-free clean bench by diluting some given amount of clean mother solution into the dust-free PC solvent.

Our laser light scattering was equipped with Brookhaven detector, Brookhaven digital correlator (model BI-9000AT), and Ar-ion laser (Lexel model 95) operated with the $\lambda_0 = 514$ nm line. Its more details are described in elsewhere.¹⁹ All experiments were measured at 25 °C.

Results and Discussion

First, the time correlation function (TCF) of the most dilute PVDF concentration of $C = 5.4 \times 10^{-7}$ g/mL is discussed. In Figure 1, our TCF has shown very different characteristics such as: (i) coupling of an exponential function with a sine wave function, (ii) very short relaxation time of only a few ms for the exponential function (iii) a prolonged appearance of sine wave function up to the measured baseline channel of 200 ms, and (v) the higher the PVDF concentration, the weaker the sine wave character in TCF. Furthermore it is also observed that all the sine wave functions have the same period (38.8 ± 0.2 ms) and the same phase (1.58 ± 0.06 rad.) regardless of PVDF concentration. Fortunately such periodic fluctuation is depressed a lot just at $C = 1.3 \times 10^{-6}$ g/mL as shown in Figure 1(c) and completely disappeared at $C > 5 \times 10^{-6}$ g/mL. Later it was found that this sine wave fluctuation came from the laser beam

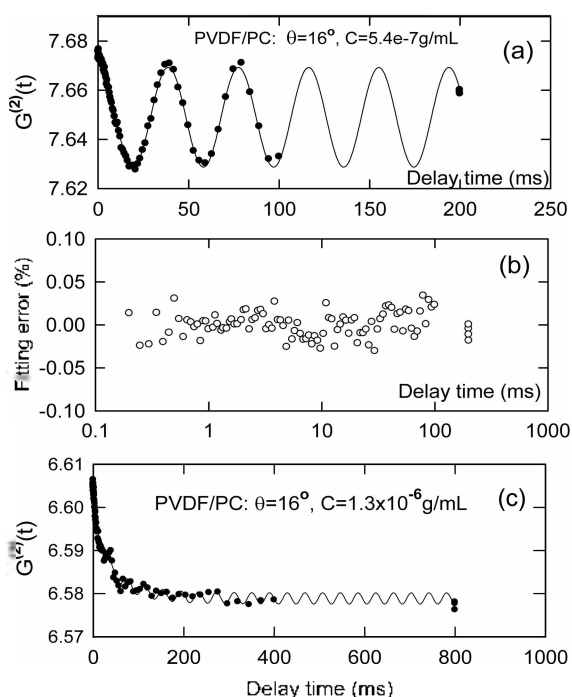


Figure 1. Time correlation function of PVDF in propylene carbonate solution at two different concentrations and the relative fitting error. As increasing polymer concentration from 5.4×10^{-7} g/mL to 1.3×10^{-6} g/mL, the sine wave character of TCF has become abruptly weak but the relaxation time has increased more than 6 times. The random and very small fitting error supports that our TCF can be fitted as the sum of a single exponential and a sine wave function.

unstability due to thermal lensing. As it appears prominently in PVDF/PC solution treated thermally at high temperature of 170 °C for complete dissolving of crystalline PVDF (melting point ~ 165 °C), we guess that the decomposition of small amount of PC solvent makes this effect. A noticeable point is that the period and amplitude of sine wave fluctuation depends on history of thermal treatment. Usually the longer treatment of more than 1 hr makes shorter period and larger fluctuation. And this wave fluctuation becomes more severe at low scattering angle of $\theta < 20^\circ$ but at high scattering angle it almost disappears.

Thus all the TCF's with sine wave character were analyzed using the equation given as:

$$G^{(2)}(t) = y_0 + a \exp(-t/b) \cdot c \cdot \sin(2\pi t/d + e) \quad (1)$$

where t means the delay time. The coefficients of a and b denote the amplitude of exponential term of chain's diffusive behavior, and the relaxation time whose reciprocal value becomes the twice of the characteristic linewidth Γ in our self-beating experiment. Although the usage of a simple single exponential in eqn. (1) surely brings some error in the determination of relaxation time b due to our polymer's polydispersity of $M_w/M_n \sim 2$, it is not also a correct way to apply mathematically more complicate exponential function to TCF of such poor signal to noise. Thus we chose the single exponential analysis method for the simplicity of calculation.

The relative fitting error, which is calculated by dividing the difference between the experimental and the calculated value with the experimental one, are shown in Figure 1(b). Such good fitness of less than 0.05% supports indirectly that eqn.(1) can be applicable. Even if the experimental situation looks very difficult and tough at the first glance, the reliable relaxation time b can be obtained under the following experimental strategy: (i) Solvent PC has large viscosity ($= 2.5$ c.p. at 25 °C) compared with regular solvent (for example, this value is corresponding to 2.8 times of that of water). (ii) By using the smallest scattering angle of $\theta = 16^\circ$, the value of q^2 ($\theta = 16^\circ$) can be reduced by 3.5 times when compared with the ordinary low angle of $\theta = 30^\circ$, where the scattering vector q is defined as $4\pi \sin(\theta/2)/\lambda_0$. It gives higher scattered intensity and makes the delay time of first channel longer. (iii) Finally, instead of losing some information at the initial stage of TCF, the first delay time is set to have longer value by 20 times than the ordinary one. Finally the first delay channel can be extended up to $\sim 100 \mu s$ and this extension effect makes much faster accumulation of TCF. Finally a reasonable TCF can be obtained even in such extremely low concentration. Of course, at the behind of the collection of this TCF, the laser power increases to ~ 400 mW and the accumulation time per each TCF is set to the order of 1 hour which is ~ 10 times longer than the regular time scale of 5 minutes.

Here, the effective s/n ratio can be defined as $a/2c$ where a and c are expressed in eqn. (1). At $C = 5.4 \times 10^{-7}$ g/mL and $\theta = 16^\circ$, the value of s/n becomes $0.17 = (7.6775 - 7.670) / (2 \times 0.021)$ but at $C = 9.4 \times 10^{-7}$ g/mL and $\theta = 16^\circ$, this increases approximately twice from 0.17 to $0.38 = (0.009 / 0.024)$. Figure 2 shows us that effective s/n is proportional to the concentration in the range of $C < 1.3 \times 10^{-6}$ g/mL. but above this concentration the value of s/n increases very rapidly. It reaches the value of $s/n \sim 2300$ at $C \sim 1.7 \times 10^{-6}$ g/mL. Since this sine wave fluctuation surely disappears above $C = 5 \times 10^{-6}$ g/mL, the second order cumulant method²⁰ is simply applied to get the characteristic linewidth Γ . Here $\Gamma(q)/q^2$ of the low scattering angle of $\theta < 30^\circ$ can be approximately

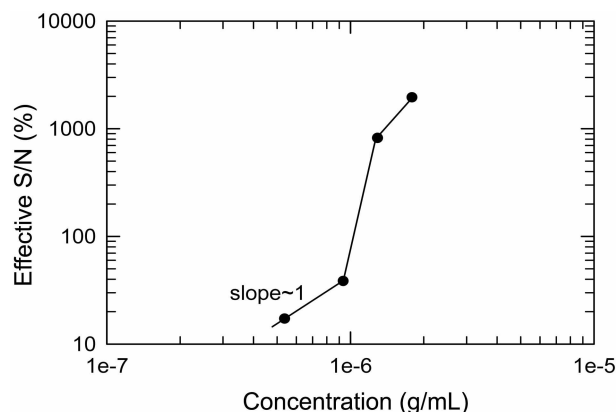


Figure 2. Plot of the effective signal to noise ratio as a function of PVDF concentration. Here the value of S/N stands for the ratio of the amplitude of exponential function to the twice of the amplitude of sine wave function in eqn. (1).

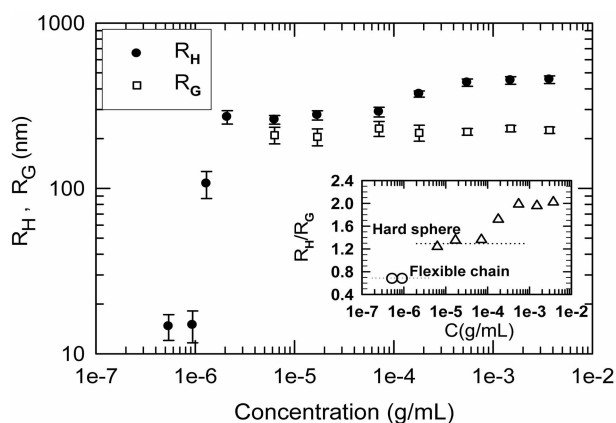


Figure 3. Plots of the radius of gyration and the hydrodynamic radius as a function of PVDF concentration. The critical aggregation concentration of PVDF can be regarded as $\sim 1.5 \times 10^{-6}$ g/mL. The ratio of R_H/R_G has been plotted against the PVDF concentration at the inserted graph where the open circle symbols of flexible chains are not experimental values but theoretical ones.

considered as translational diffusion coefficient D_o . The effective hydrodynamic radius R_{H1} is calculated using Stokes-Einstein equation of $R_{H1} = k_B T / 6\pi\eta_o D_o$, where k_B and η_o mean Boltzmann constant and solvent viscosity, respectively. As the static size, the radius of gyration R_G is calculated from the excess scattering intensity I_{ex} using Guinier equation²¹ of $I_{ex} = I_o \exp(-R_G^2 q^2/3)$. Although dynamic light scattering is possible even at very dilute concentration through a variety of techniques above-mentioned, it is impossible in static light scattering to get reliable the excess scattered intensity I_{ex} below $C = 5 \times 10^{-6}$ g/mL. Thus the apparent value of R_G is calculated only at $C \geq 5 \times 10^{-6}$ g/mL.

Figure 3 has shown us how R_{H1} and R_G depend on the concentration at wide range of PVDF concentration. It is noticeable that especially at $C \leq 1 \times 10^{-6}$ g/mL, the hydrodynamic radius keeps constant as $R_{H1} \sim 15$ nm which seems to be corresponding to the size of a single chain. Using the Mark-Houwink equation of PVDF/acetophenone system at 85 °C, $[\eta] = 2.13 \times 10^{-2} M_w^{0.02}$, the intrinsic viscosity of our sample with M.W. = 534,000 g/mol becomes the order of $[\eta] = 75.8$ mL/g. If one step goes further for the viscometric radius $R_v (= (3M_w[\eta]/10\pi N_A)^{1/3})$, the R_v value is calculated as 18.6 nm, which shows good agreement with our value of $R_{H1} \sim 15$ nm. Thus it is our conclusion that the PVDF polymer exists as a separated single chain of the flexible conformation below $C = 1 \times 10^{-6}$ g/mL. This result is also comparable with Chu's result²² that poly(tetrafluoroethylene) of M.w. = 2.9×10^5 g/mol has the flexible chain conformation of $R_G = 17.8$ nm in poor solution state. Next, when the concentration increases from 1×10^{-6} g/mL to 2×10^{-6} g/mL, the hydrodynamic radius of PVDF increases abruptly from ~ 15 nm to ~ 270 nm. Such increase of R_{H1} supports the existence of a critical aggregation concentration (CAC) above which PVDF polymers can no longer exist as a single flexible chain but form large aggregates due to their strong attractive interaction. The CAC of this system is

determined as $\sim 1.5 \times 10^{-6}$ g/mL. The following question is what is the driving force for this kind of aggregation. As reported in previous paper,¹⁷ according to ^{19}F NMR analysis²³ of our PVDF sample, the amount of A7 sequence (=0101010 sequence) has occupied about 81% among total heptads. Here as 0 and 1 denote head and tail configuration, respectively, the configuration of A7 consists of four consecutive heads and 3 consecutive tails. But it is found that B7 (=0101011), C7 (=1001010), and E7 (=0101100) have 5.0%, 4.8% and 4.6%, respectively. According to Wilson's report of fluoropolymer,^{24,25} a mesophase was observed in a series of fluorinated esters where the fluoroalkyl mesogenic unit was very short (for example, 4 carbon atoms in length). And he explained that the fluorinated part of at least four carbon atoms could play as the driving force of this mesophase formation. Thus on the basis of our result of heptad sequence analysis of PVDF, it can be assumed that in our experiment of very dilute concentration, four consecutive sequences of head-to-tails may play a role as a driving force for aggregation compared to a randomly mixed sequence of head-to-tail and head-to-head (or tail-to-tail). It has been already confirmed by laser light scattering experiment that this strong attractive interaction makes PVDF chains form the core-shell structure above $C = 1 \times 10^{-4}$ g/mL. Just above the CAC, the ratio of R_{H1} to R_G keeps as 1.28 which is a well-known ratio of hard sphere. In other words, around $C \sim 6 \times 10^{-6}$ g/mL ($\sim 4 \times CAC$), many polymer chains form a spherical aggregate having the uniform monomer density inside. However as this value of $R_{H1}/R_G = 1.28$ is just transient, this ratio increases with increasing concentration and finally reaches a plateau value of $R_{H1}/R_G \sim 2.0$ above $C = 5 \times 10^{-4}$ g/mL.

Here, as one of possible structures for the final stage of this aggregate, a linear gradient density model can be considered where the center of aggregate is filled with only monomer units (*i.e.* $\rho = 1$) and then this monomer density is linearly decreasing down to $\rho = 0$ at the edge. In this situation, the theoretical value of R_{H1}/R_G is calculated using the following equation.¹⁶

$$R_{G1}^2 = \frac{\int_0^R r^2 \rho(r) 4\pi r^2 dr}{\int_0^R \rho(r) 4\pi r^2 dr} \quad (2)$$

If the linear relation between density and position variable r at the range of $0 \leq r \leq R$ can be expressed as $\rho(r) = 1 - r/R$, finally R_{G1}^2 is obtained as $(12/30)R^2$ and then R_{H1}/R_G becomes 1.58. Thus to get such large value of $R_{H1}/R_G > 1.8$, the most suitable model for the structure of aggregate is core-shell type. It has already reported by Park¹⁷ that the light scattering intensity pattern calculated from the core-shell structure of aggregate shows very good agreement with the experimentally observed one. Based on this core-shell model, it is found that the relative monomer density of shell part reaches only 7% of the core part density level.

Overall, PVDF exists as a single flexible chain at the very dilute concentration but just above CAC, in the initial stage of aggregation, the fraction part of A7 sequence in PVDF

chain forms hard spheres of uniform density. If the concentration increases further, the structure of hard sphere should be transformed into the core-shell form. In this process the former hard sphere becomes a compact core part and additionally aggregated polymer chains form the shell part. Although we did not try to do gelation experiment in this study, it was reported in many previous papers that the gel formation concentration, C_{gel} was the order of 1-2 wt%.^{10,11} This concentration is almost corresponding to the contact-beginning (=overlap) concentration of the core radius of ~220 nm. For example, based on the previous molecular weight ($\sim 5 \times 10^8$ g/mol) of aggregate particle,¹⁷ the overlap concentration C^* ($\sim M_w / (4\pi R_H^3 N_A / 3) \sim 1.8$ wt%) is the same order of experimental gel formation concentration.

In conclusion, as far as we have known, we report first that there exists a critical aggregation concentration in very dilute PVDF solution and that at the initial stage of aggregation it shows hard sphere-like structure but later it converts into the core-shell structure. And then the gel formation concentration seems to be dependent basically on the core size rather than the overall size of the particle. Our future work will be concentrated on how the core-shell structure is subject to some factors such as the solvent power and the amount of the consecutive sequence of head-to-tail configuration.

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