Magnetic field induced uniaxial alignment of the lyotropic liquid-crystalline PMMA-grafted Fe$_3$O$_4$ nanoplates with controllable interparticle interaction

Chen Shen, Masaki Matsubara, Mizuho Yabushita, Sachiko Maki, Atsushi Muramatsu, Kiyoshi Kanie

$^a$Institute of Multidisciplinary Research for Advanced Material, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan.
$^b$National Institute of Technology, Sendai College, 48 Nodayama, Medeshima-Shiote, Natori, Miyagi 981-1239, Japan.
(E-mail: kanie@tohoku.ac.jp)

1. Determination of modification densities on Fe$_3$O$_4$

1.1 Calculation of modification densities of amine groups and SI-ATRP initiators on Fe$_3$O$_4$

Modification amounts of amine groups and SI-ATRP initiator-modified Fe$_3$O$_4$ were determined by TA. The TA measurements were carried out under Ar gas, and the heating ratio was fixed to 10 °C/min. Here, amine-groups modified Fe$_3$O$_4$ and SI-ATRP initiator-modified Fe$_3$O$_4$ were abbreviated by FN and F*, respectively. Weight losses of Fe$_3$O$_4$, FN, and F* by TA measurements were abbreviated as $L_{FN}$, $L_{FN}$, and $L_{LF}$, respectively. The modification density of amine groups on Fe$_3$O$_4$ was calculated by the following equation (eq. S1). Here, $N_A$ is Avogadro constant and $S_{AES}$ is the estimated specific surface area of Fe$_3$O$_4$. The measurement result of $S_{AES}$ is 14 m$^2$/g. $MW_a$ means a molecular weight of organic moieties on Fe$_3$O$_4$. In this case, we subtracted molecular weight of trimethoxysilyl group from molecular weight of N-[3-(trimethoxysilyl)propyl]aniline to calculate $MW_a (MW_a = 134)$.

\[
\text{Amine - groups modification density} = \frac{N_A \left( \frac{L_{FN}}{100 - L_{FN}} - \frac{L_F}{100 - L_F} \right)}{S_{AES} \times MW_a} \text{ chains/nm}^2 \quad \text{eq. S1}
\]

Next, SI-ATRP initiator modification densities ($D_i$) on Fe$_3$O$_4$ were calculated by the following equation (eq. S2 and S3). Here, $x$ means reaction rate of amine groups in the initiator modification and $y$ means amine groups modification amount for 1 g of Fe$_3$O$_4$. $MW_b$ means a molecular weight of organic moieties on Fe$_3$O$_4$ which subtracted molecular weight of trimethoxysilyl group after reacting with BBI ($MW_b = 401$).

\[
x \cdot y \cdot MW_b + (1 - x) \cdot y \cdot MW_a = \frac{L_{F*}}{100 - L_{F*}} - \frac{L_F}{100 - L_F}
\]

\[
y = \frac{\left( \frac{L_{FN}}{100 - L_{FN}} - \frac{L_F}{100 - L_F} \right)}{MW_a}
\]
\[
x = \frac{L_{F^*}}{100 - L_{F^*}} - \frac{L_F}{100 - L_F} - y \cdot MW_a \cdot \frac{y \cdot (MW_b - MW_a)}{SA_{ES}}
\]

eq S2

\[
D_T = x \cdot y \cdot \frac{N_A}{SA_{ES}} \text{chains/} \text{nm}^2
\]

eq S3

Fig. S1 shows TA profiles of F, amine-groups modified F, and SI-ATRP initiator-modified F.

1.2 PMMA modification densities

Modification amounts of PMMA were also determined by TA. Weight of PMMA for 1 g of F was marked as \(W_{FP}\). Here, \(L_{FP}\)% is weight loss of \(FP_m\) (\(m = 1, 2, 3\)).

\[
W_{FP} = \frac{L_{FP}}{100 - L_{FP}} - \frac{L_{F^*}}{100 - L_{F^*}} - \frac{L_F}{100 - L_F}
\]

eq S4

Next, PMMA modification densities (\(D_p\)) were calculated by the following equation (eq. S5). \(Mn\) means number average molecular weight of PMMA on F, which was determined by SEC.

\[
D_p = \frac{W_{FP}}{Mn} \cdot \frac{1}{SA_{ES}} \text{chains/} \text{nm}^2
\]

eq S5

Fig. S2 shows TA profiles of \(FP_m\).
1.3 Calculation results

The $D_I$ values, $D_P$ values and molecular weight distribution were listed in Table. S1. The weight fractions ($F_w$) and volume fractions ($F_v$) mean the proportion of PMMA chains' weight and volume in overall $FPm$, respectively.

|       | $M_w/M_n$ | $D_I^a$ | $D_P^b$ | $F_w^c$ | $F_v^d$ |
|-------|-----------|---------|---------|---------|---------|
| FP1   | 1.17      | 0.17    | 0.11    | 0.35    |         |
| FP2   | 1.27      | 1.85    | 0.26    | 0.29    | 0.64    |
| FP3   | 1.43      | 0.37    | 0.37    | 0.44    | 0.77    |

$^a$Modification densities of SI-ATRP initiator, $^b$modification densities of PMMA, $^c$weight fraction of PMMA and $^d$volume fraction of PMMA.

2. FT-IR

Fig. S3 shows the FT-IR spectra of $F$, $FP3$, and PMMA. In the spectra of $FP3$ as shown in Fig. S3b, the peaks at 2999 cm$^{-1}$ and 2947 cm$^{-1}$ are assigned to the C-H bond, and the peaks at 1724 cm$^{-1}$ are attributed to the C=O bond of PMMA. The FT-IR results indicate that large quantities of PMMA were grafted on the surface of $F$.

![Fig. S3 FT-IR spectra of (a) F, (b) FP3, and (c) PMMA.](image)

3. POM

POM observation was utilized to observe the lyotropic LC phases of $FPm$ in ionic liquids. As is shown in Fig. S4a, only black images were observed because of the color of $F$ and the not long enough PMMA chains. Fig. S4b exhibit the POM images of $FP3/[Emim^+][NTf_2^-]$ (weight ratio: 1/3) at 200 °C. Optical birefringence could be observed due to the formation of the lyotropic nematic phases even though were heated to 200 °C from room temperature. However, obvious birefringence was not observed in other $FP3/[Emim^+][NTf_2^-]$. 

![image]
Fig. S4 POM images of (a) FP1/[Emim][NTf₂⁻] (weight ratio: 1/2) , (b) FP3/[Emim⁺][NTf₂⁻] (weight ratio: 1/3) at 100 °C. The scale bar shown in (b) is common for both of the two images.

4. Sketches of dripping FP3/toluene solution under magnetic field

A drop of FP3/toluene solution (concentration: 0.1 g/L) was dripped on a TEM grid after applying an external magnetic field that was vertical or parallel to the TEM grid.

Fig. S5 Sketches of dripping FP3/toluene solution under a vertical magnetic field (a), or a parallel magnetic field (b).

5. TEM image of F under a vertical magnetic field

A drop of F/toluene solution (concentration: 0.05 g/L) was dripped on a TEM grid after applying an external magnetic field that was vertical to the TEM grid. Most of F lay vertically along the magnetic field direction as is shown in Fig. S6.

Fig. S6 TEM image of F under a vertical magnetic field.
6. Interparticle distance of FP under an external magnetic field.

The interparticle distance results of FP1, FP2, and FP3 under an external magnetic field (320 Oe), obtained from the USAXS curves, were listed in the Table. S2.

Table. S2 Interparticle distance results of FP1, FP2, and FP3 under an external magnetic field (320 Oe).

| Interparticle distance (nm) |
|-----------------------------|
| FP1            | 180 |
| FP2            | 184 |
| FP3            | 195 |