Electronic Supplementary Information

Dispersion of Carbon Nanotubes Triggered by Helical Self-assembly of Poly(methyl methacrylate)

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Supplementary Results

NMR for the determination of PMMA's tacticity.

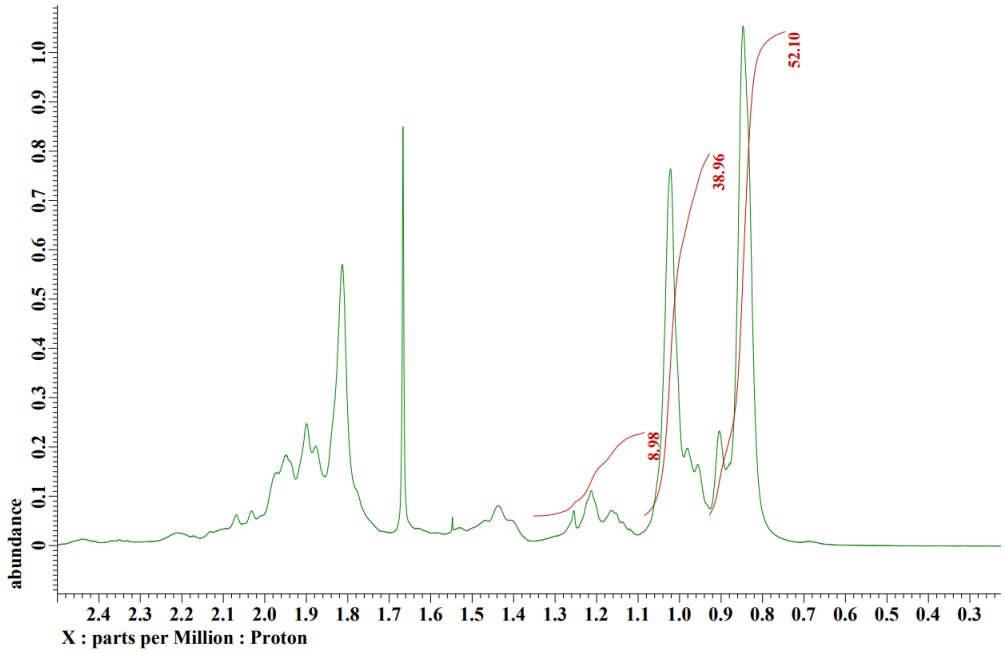

Figure S1. ^{1}H-NMR chart of syndiotactic PMMA (r=72) in $CDCl_3$.

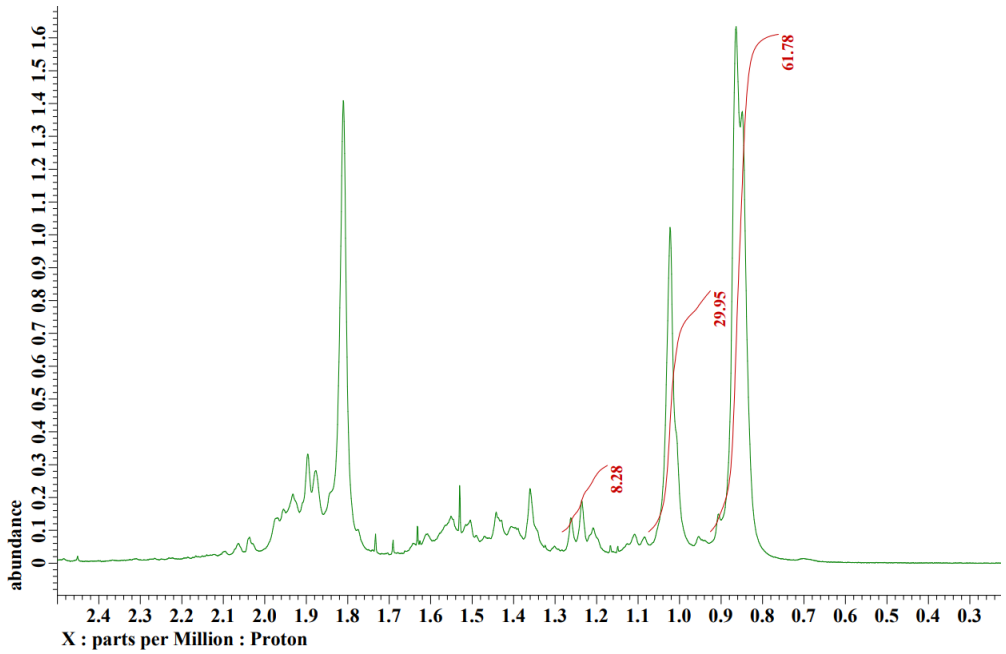

Figure S2. ^{1}H-NMR chart of syndiotactic PMMA (r=77) in $CDCl_3$.

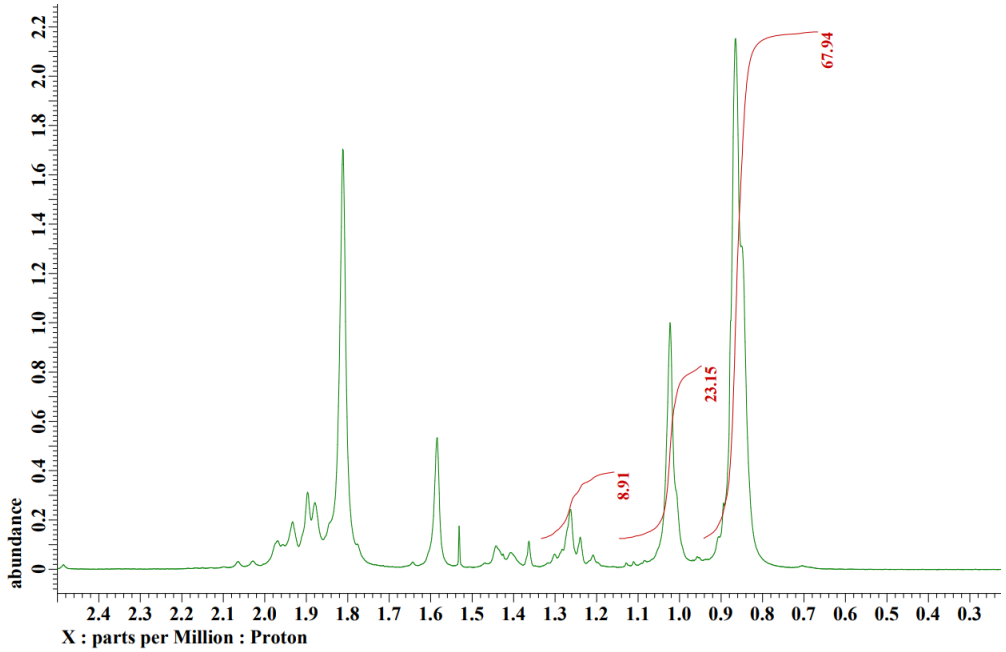

Figure S3. ^{1}H-NMR chart of syndiotactic PMMA (r=80) in $CDCl_3$.

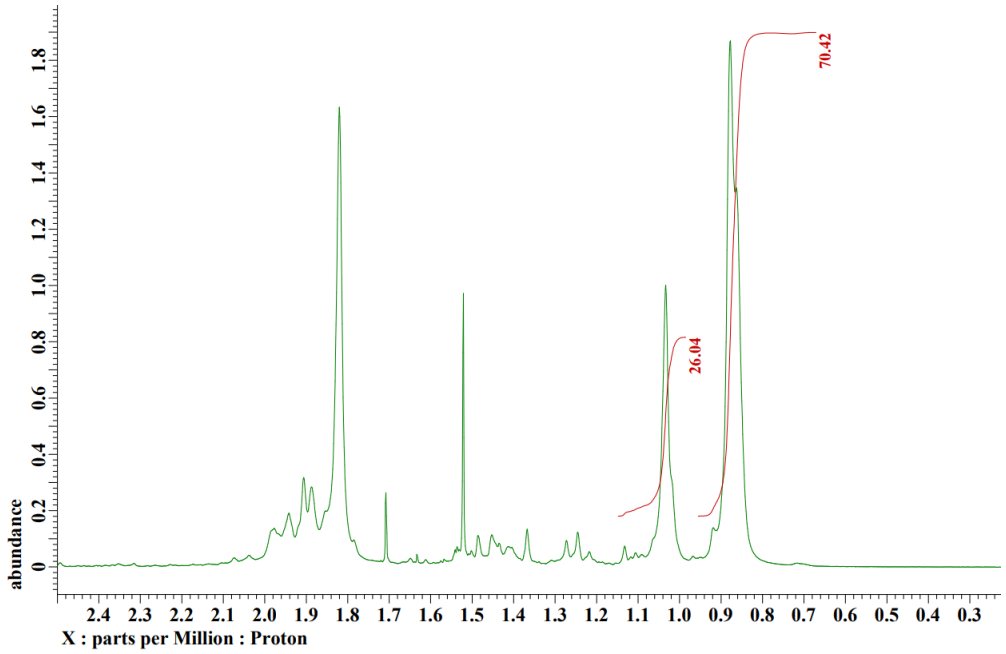

Figure S4. ^{1}H-NMR chart of syndiotactic PMMA (r=83) in $CDCl_3$.

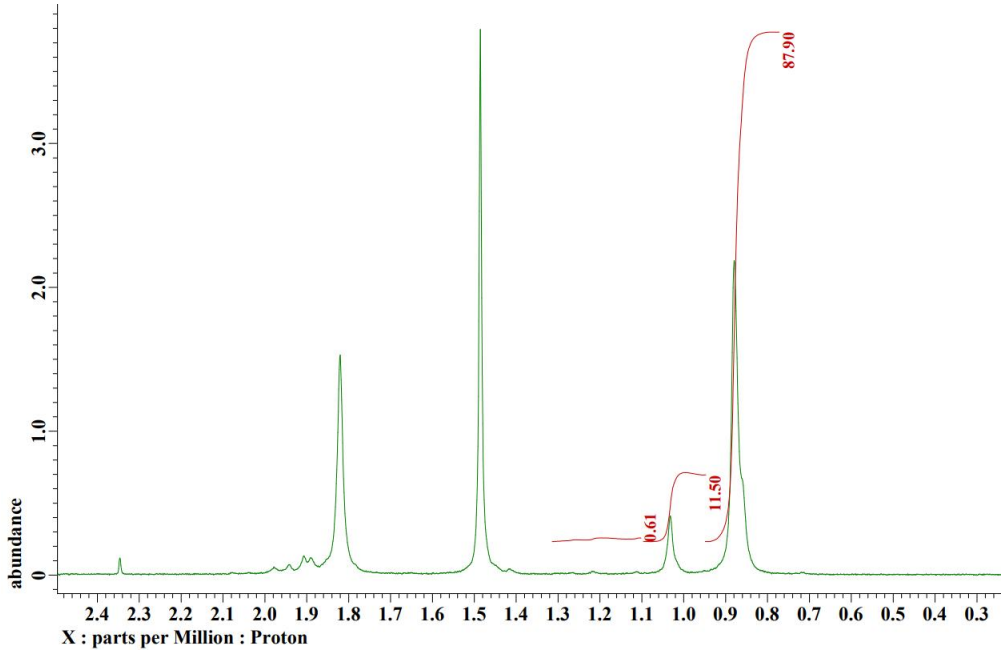

Figure S5. ^{1}H-NMR chart of syndiotactic PMMA (r=92) in $CDCl_3$.

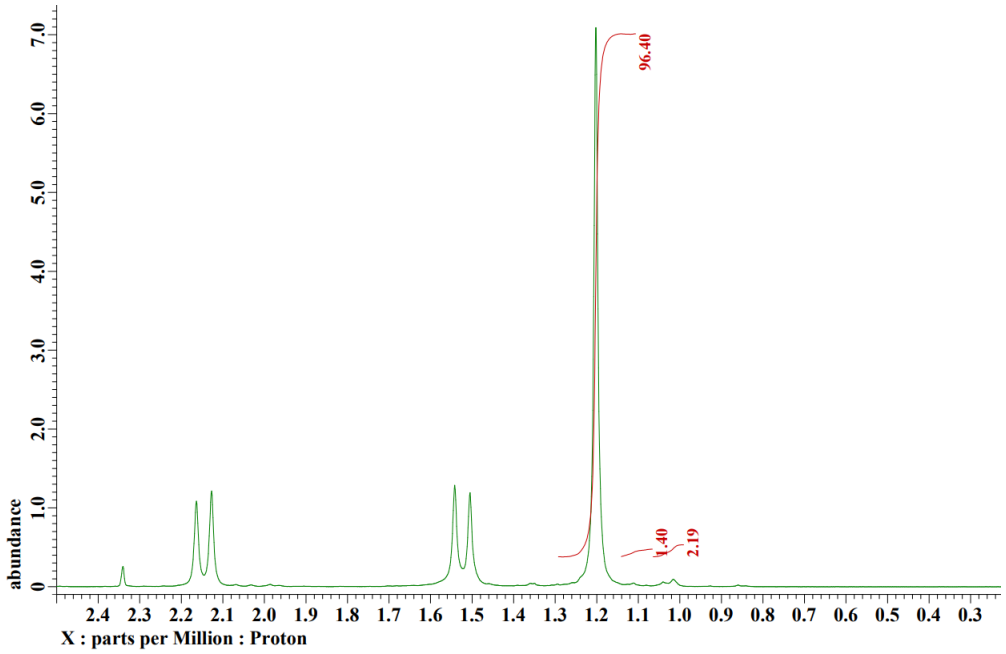

Figure S6. ^{1}H-NMR chart of isodiotactic PMMA (m=97) in $CDCl_3$.

Absorption spectra for various helical polymers and organic solvents

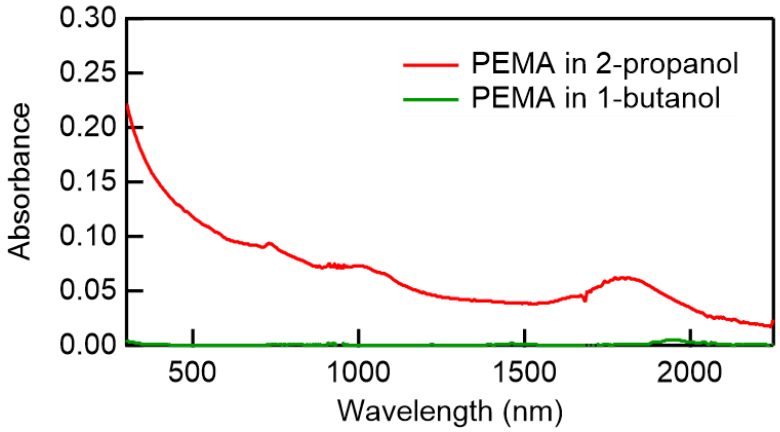

Figure S7. Absorption spectra of arc-SWCNTs with poly(ethyl methacrylate) (PEMA) in 2-propanol and 1-butanol.

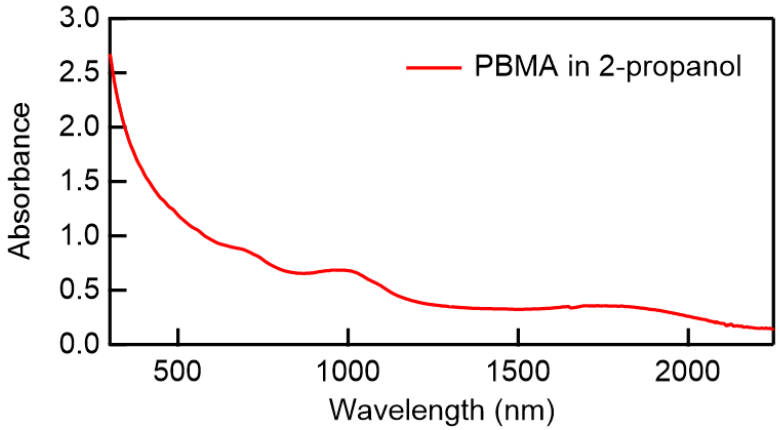

Figure S8. Absorption spectra of arc-SWCNTs with poly(butyl methacrylate) (PBMA) in 2-propanol.

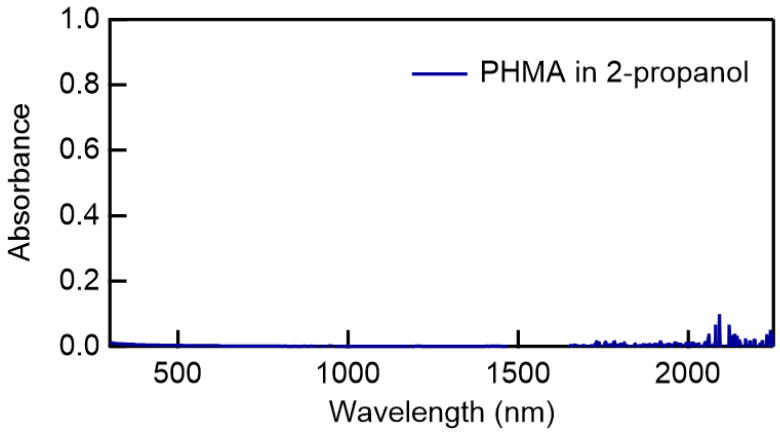

Figure S9. Absorption spectra of arc-SWCNTs with poly(diphenyl-2-pyridylmethylmethacrylate) (PHMA) in 2-propanol.

Experimental and computational methods

Computational details

We performed density functional theory (DFT) calculations under periodic boundary conditions (PBC), as implemented in the Vienna Ab-initio Simulation Package (VASP v.6.3.0) code, [S1,S2] to investigate whether a helical syndiotactic poly(methyl methacrylate) (st-PMMA) can wrap a carbon nanotube. As the correlation and exchange functional in the DFT calculations, we used the generalized gradient approximation (GGA) with the functional by Perdew-Burke-Ernzerhof (PBE).[S3] To properly estimate long-range interactions between a tube and st-PMMA, we added empirical dispersion correction to PBE functional (DFT-D3 method), based on Ref. S4, developed by Grimme et al. The ion-electron interaction was described with the projected augmented wave (PAW) method.[S5] For the plane-wave basis set, a cutoff energy of 500 eV was used.

We used a hexagonal supercell with dimensions 40 × 40 × 14.814 Å in the (7,7) tube, st-PMMA, or (7,7) tube wrapped by st-PMMA (denoted by (7,7)@st-PMMA). The supercell is sufficiently large to avoid interactions between models in the adjacent supercells. Using these models, we fully optimized atomic configurations in the (7,7) tube, st-PMMA, and (7,7)@st-PMMA, whose cell parameters were fixed, and then obtained local minima. In the supercell calculations, the Brillouin zone sampling was restricted to only the Γ point, and energies were converged with a 1×10^{-5} eV tolerance. We judged that the optimizations converged when the maximum forces on all atoms are less than 0.03 eV/Å. After obtaining optimized structures, we calculated the stabilization energy ($E_{\text{stabilize}}$) of (7,7)@st-PMMA, defined as follows

$$E_{\text{stabilize}} = E_{\text{total}}((7,7)@\text{st-PMMA}) - E_{\text{total}}((7,7)) - E_{\text{total}}(\text{st-PMMA})$$

Here, $E_{\text{total}}((7,7)@\text{st-PMMA})$, $E_{\text{total}}((7,7))$, and $E_{\text{total}}(\text{st-PMMA})$ represent the total energies of (7,7)@st-PMMA, an (7,7) tube, and st-PMMA, respectively.

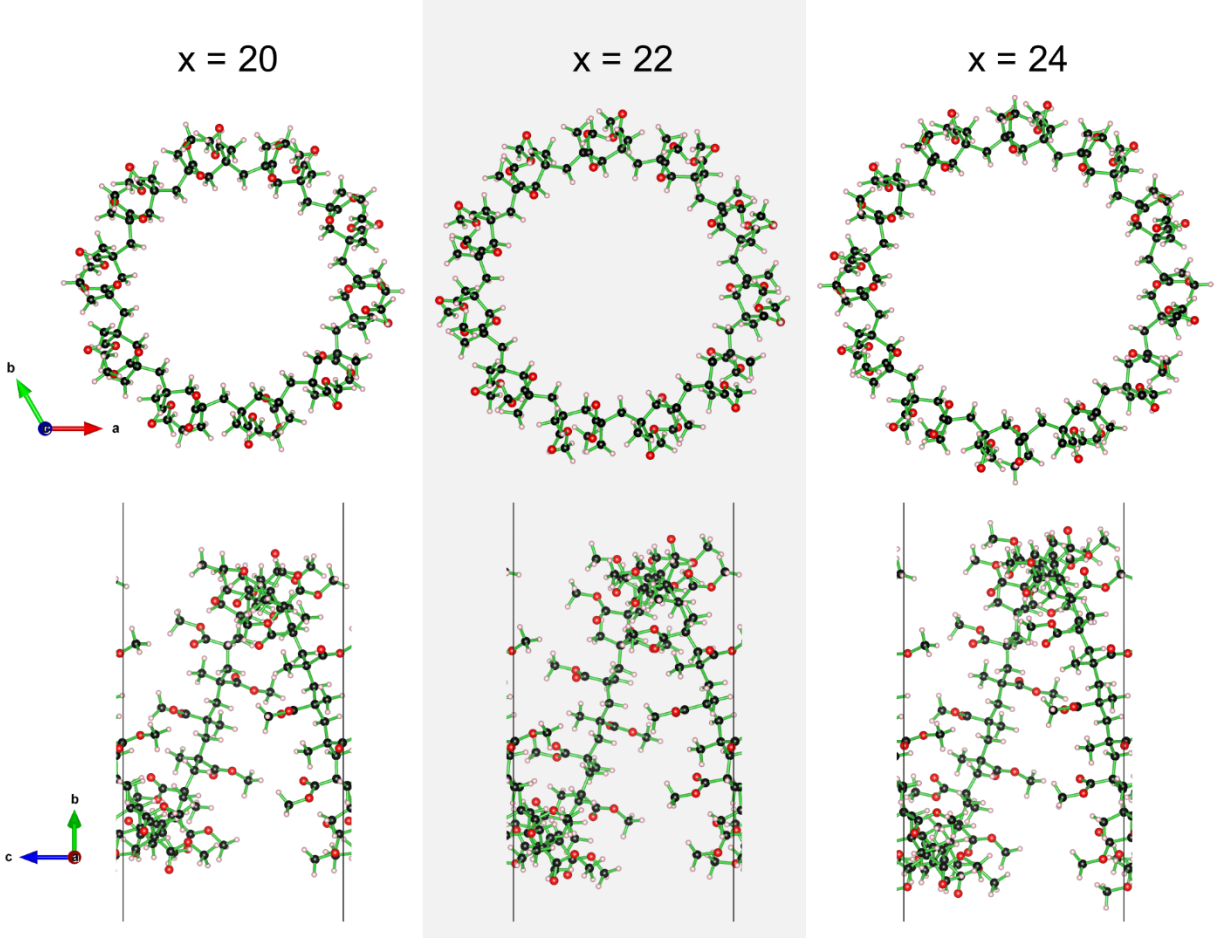

Figure S10. Optimized structures of syndiotactic PMMA for various helical pitches in the unit cell. For $[MMA]_x$, x indicates the number of MMA that can form one pitch.

Materials and methods

We used single-walled carbon nanotubes as received, purchased from Merck (Sigma-Aldrich) (CoMocat, and arc-discharge), NoPo (Hipco), OCSiAl (Tuball of two different batch #53-15122014 and #01RW02.N1.208), and kindly supplied from Osaka Soda (eDIPS EC2.0). Dry tetrahydrofran and dry acetonitrile were purchased from Kanto Chemical. Toluene, 1-butanol, and 2-propanol were purchased from Wako Pure Chemical Industries. 2-heptanone was purchased from Nacalai Tesque. Radically polymerized PMMA (r~65) and isotactic PMMA (m~97, M_w: 1.42×10^5, M_w/M_n: 1.71.) were purchased from Merck (Sigma-Aldrich). Syndiotactic PMMA (Syndiotactic >85%, practically measured r~92, M_w: 1.07×10^5, M_w/M_n: 2.05) was obtained from Polymer Source inc. (Canada).

Absorption spectra were recorded using the UV-Vis-NIR absorption spectrophotometer with PMT, InGaAs, and PbS detectors (Shimadzu UV3600plus) with 10 mm quartz

cuvettes (GL Science S15-IR-10). NMR spectra were obtained using JEOL JNM-ECX400P. The molecular weight distribution was estimated using gel permeation chromatography (Shimadzu Prominence/LC-20AD system). Transmission electron microscopy was conducted using JEOL JEM-3100FEF with high resolution-type carbon-coated Cu microgrid (Ouken Shoji).

Radical polymerization of MMA to PMMA in HFIP.

Methyl methacrylate (MMA) (5.35 mL, 50 mmol) was passed through an alumina column to remove the polymerization inhibitor; MMA, 2, 2'-azobisisobutyronitrile (AIBN) (205.7 mg, 1.25 mmol), hexafluoro-2-propanol (HFIP) (19.5 mL) were added to a Schlenk tube and stirred well; an LED light source was set and oxygen was removed from the system by bubbling the reaction solution with nitrogen. The reaction was stirred for 24 h. After the UV light irradiation was terminated and the reaction stopped, the polymerization solution was dropped into a large volume of hexane to precipitate the polymer formed. The supernatant solution was removed by the gradient method and the surface was washed with hexane. Suction filtration gave the white powder (0.28 g, 5% yield). M_w: 2.46×10^4, M_w/M_n: 1.58.

Radical polymerization of MMA to PMMA in HFIP.

The synthesis was performed by the simiar manner above, except for the use of dry tetrahydrofran (THF) (0.93 g, 19% yield). M_w: 1.21×10^4, M_w/M_n: 2.57.

Determination of tacticity of PMMA

In the 1H NMR spectrum, the three signals of α-methyl protons of PMMA can be attributed to mm:mr:rr from the high field side in the range of 1.0–1.3 ppm . The relationship between the binary and ternary signals is expressed by the following equation.

$$\mathrm{m} = \mathrm{mm} + \frac{1}{2}mr$$

$$\mathrm{r} = \mathrm{rr} + \frac{1}{2}mr$$

The tacticity of the four types of st-PMMA was determined as a binary (m:r) from the integral ratio of the peaks corresponding to mm:mr:rr.

References

S1 J. Furthmüller, J. Hafner, and G. Kresse, *Phys. Rev. B*, 1994, **50**, 15606.

S2 G. Kresse and J. Furthmüller, *Computational Materials Science*, 1996, **6**, 15.

S3 J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.*, 1996, **77**, 3865.

S4 S. Grimme, J. Antony, S. Ehrlich, and S. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104.

S5 P. E. Blöchl, *Phys. Rev. B*, 1994, **50**, 17953.