

pubs.acs.org/JPCB

Article

Molecular Disaggregation Process of PTFE Using Sodium Chloride: A Study by Infrared Spectroscopy

Tomoya Oonuki, Taisuke Araki, Takayuki Oka, Hiroshi Matsuda, Nobutaka Shioya, Junya Kano, Akihide Hibara, and Takeshi Hasegawa*



ABSTRACT: Mechanical recycling of polytetrafluoroethylene (PTFE) has long been a crucial matter in fluorocarbon chemistry. Since the molecular aggregation of PTFE is outstandingly strong, fluorocarbon solvents are believed to be necessary for the disaggregation of PTFE, but they should not be used as much as possible because of concerns about environmental impact. Recently, a new technique using solid sodium chloride with the aid of planetary ball milling, instead of using fluorocarbon solvents, has been proposed, and this simple technique works powerfully indeed for the purpose, as confirmed by a significant decrease of crystallinity. Here, we show that the molecular disaggregation process of PTFE using sodium chloride is revealed in detail by infrared (IR) spectroscopy. The spectra clearly show that PTFE is readily crushed into fine particles, and molecular disaggregation within the particles is also recognized. These changes are not found at all in a process that does not use sodium chloride. In addition, the generation of helical defects in perfluoroalkyl chains is also found, which is correlated with molecular disaggregation. In this manner, IR spectroscopy has been found to be a useful tool in providing us rich information on the molecular disaggregation process of PTFE across three different hierarchical structures.

■ INTRODUCTION

See https://pubs.acs.org/sharingguidelines for options on how to legitimately share published articles.

Downloaded via 133.3.201.34 on May 15, 2025 at 06:51:37 (UTC).

Perfluoroalkyl (R_f) compounds^{1,2} have unique material characteristics, represented by water/oil repellence and low electric permittivity,^{3,4} that cannot be regenerated by hydrocarbons without using fluorine. The history of organofluorine chemistry dates back to the unexpected, coincidental synthesis of polytetrafluoroethylene (PTFE), revealed by Plunkett in 1938.⁵ Even in the very early stages of organofluorine research, PTFE was already recognized to be very unique not only in material characteristics but also in the difficulty of processing the material block. Reshaping PTFE blocks is indeed highly difficult because the molecular disaggregation of PTFE is quite difficult.² This difficulty is partly due to the molecular entanglement commonly found in polymers, but intrinsically due to the R_f-specific, uniquely strong molecular interaction because of the strong dipole-dipole interaction.⁶⁻¹² To make the reshaping process easier, branched structures and hydrophilic chemical groups are introduced into the primary chemical structure by reducing the molecular interactions.

Through these efforts and challenges, many useful materials were developed, including Nafion, which is an essential material for the fuel cell technology.^{13–17}

In this manner, R_f compounds have long been developed by making efforts to enable easy disaggregation of molecules for softening the materials. It has already been shown theoretically, with a number of experimental supports, that the R_f -specific material characteristics are the result of uniquely strong molecular interactions due to dipole–dipole interactions.^{11,12} At the same time, unfortunately, the strong intermolecular

Received:February 19, 2025Revised:March 30, 2025Accepted:April 2, 2025Published:April 17, 2025





Figure 1. (a) IR ATR spectra of PTFE powder measured before (blue) and after (red) the ball-milling treatment with NaCl. (b) Normalized spectra of the region #3 around the band at 638 cm^{-1} .

aggregation produces a negative side effect, as it makes mechanical recycling very difficult.

To reduce environmental impact, two different approaches, namely the "chemical" and "mechanical" recycling processes, are being studied intensively.^{18–20} "Chemical recycling" aims to decompose the matter totally and return it further back to the original raw material.² In the case of PTFE, for example, PTFE is chemically decomposed completely, and the collected fluorine atoms are returned to calcium fluoride, i.e., the source material. Although this is an extremely strong approach, it requires high energy for the recycling purpose, which creates another environmental impact.

"Mechanical recycling" is, on the other hand, another approach in which the molecular aggregates are disaggregated back to the preaggregated molecules, which requires much less energy than the chemical one. Nevertheless, PTFE has the strongest molecular aggregation property among the R_f compounds, as mentioned above, and fluorous solvent has thus long been believed to be necessary for the disaggregation purpose. However, fluorous solvents have a strong environmental impact, and their use should be avoided as much as possible.

Recently, to get over the dilemma, Hibara and coworkers have proposed the idea that fluorous solvents can be interpreted as "dipolar molecules," therby expanding the concept of solvents.²¹ With this expanded concept, they boldly chose sodium chloride as a solvent-ish additive instead of using fluorous solvents. The ionic pair of Na⁺ and Cl⁻ can indeed be recognized as having a strong permanent dipole moment. Nevertheless, a single molecular sodium chloride is not available. Instead, crushed fine powder particles of sodium chloride have multipolar characteristics that are good enough to "solvate" PTFE molecules. As a matter of fact, they showed clearly that PTFE was transformed into a fine powder—one that had never been seen before—only by adding sodium chloride.

In the present study, the molecular disaggregation process has been analyzed in detail by using infrared (IR) spectroscopy. IR spectroscopy is known to be particularly powerful for the analysis of R_f compounds. Since the R_f groups are strongly aggregated by dipole–dipole interactions, the molecular vibrations of the neighboring molecules are coupled to generate phonons that can be used for the analysis of molecular aggregation.^{8–10,22,23} In addition, IR spectra are quite sensitive to the molecular helical conformations specific to the R_f compounds^{24–28} and the molecular atmosphere via the vibrational Stark effect.^{29,30} Thanks to the good combination of IR spectroscopy and R_f compounds, the crushing process, with the aid of sodium chloride, is vividly revealed in three steps involving different hierarchical structures: 1) fine grinding of the matter, 2) molecular disaggregation in the ground powder, and 3) generation of conformational defects in individual molecules.

EXPERIMENTAL SECTION

Sodium chloride with JIS Special grade was purchased from FUJIFILM Wako Pure Chemical Corporation (Osaka, Japan) and Manac inc. (Tokyo, Japan). PTFE with Practical grade and two different molecular masses (M_m) of about 5,000–20,000 and 100,000 were purchased from FUJIFILM Wako Pure Chemical and Sigma-Aldrich (Saint Louis), respectively. They were used without further purification. After the experiments using the two samples, the high- M_m sample showed an almost identical spectrum (Figure S1) to the low M_m one. Since the high- M_m sample has a wide variation in M_m around the average mass, the low- M_m sample was employed for the discussion in this paper.

For the crushing experiments using an additive having no dipole moment, copper fine powder was used. The copper powder was supplied from Kanto Chemical Co., Inc. (Tokyo, Japan), which was a first-class reagent with a purity of 99.85% or higher. The particle size was within a range of 75 to 150 μ m.

IR Attenuated Total Reflection (ATR) Spectra Measurements. IR spectra of the powder samples were measured by the ATR technique using a PIKE Technologies (Madison, WI, USA) GradiATR single-bounce reflection attachment having an ATR prism made of diamond. The angle of incidence was fixed at 45°, and unpolarized light was used. After pressing the sample onto the ATR prism, IR measurements were performed using a Thermo Fisher Scientific (Madison, WI, USA) Nicolet iS50 FT-IR spectrometer having a deuterated triglycine sulfate (DTGS) detector with a wide wavenumber range extending down to 400 cm⁻¹. The DTGS detector was used with a modulation frequency^{22,31} of 15 kHz. Accumulation was carried out 128 times for each spectrum, and the wavenumber resolution was set to 1 cm^{-1} . The apodization function^{22,31} was set to Blackman-Harris throughout the study. All measurements were performed under ambient pressure with a dried air flow. The dried air was generated by an Anest-Iwata (Yokohama, Japan) SmartAir SLP-37EFD M6 Scroll Compressor connected with a Parker Balston (San Jose, CA, USA) 75-62 FT-IR purge gas generator.

Grinding Using a Planetary Ball Mill. PTFE mixed with sodium chloride was ground using a Fritsch (Idar-Oberstein, Germany) P-7 planetary ball mill. The vial and balls were made of zirconia. The volume of the vial was 45 mL, containing seven balls with a diameter of 15 mm. The rotation speed was

700 rpm, and the duration time of grinding was 8 h. The molar mixing ratio of the number of the CF_2 groups in PTFE to sodium chloride was 1:1 (corresponding to a mass ratio of 1:1.17), and 3 g of the mixture was charged into the mill. When PTFE alone was ground, 3 g of PTFE was charged into the mill. To remove sodium chloride from the powder, the milled sample was gently stirred in water for 5 min, followed by paper filtration, which was further dried at 50 °C overnight.

Powder X-Ray Diffraction (XRD) Measurements. Powder XRD measurements were performed on a Rigaku (Tokyo, Japan) SmartLab X-ray diffractometer. Cu K α radiation (λ = 0.15418 nm) was generated from a sealedtube X-ray source operated at 50 kV and 40 mA. The convergent beam was irradiated on the surface of a well-ground sample, and the scattered rays were detected by a Rigaku HyPix-3000 hybrid pixel counting detector at scattering angles, 2θ . Measurements were performed twice for individual samples: the first set, aimed at obtaining the entire diffraction pattern, employed a scanning rate of 4 min⁻¹ with steps of 0.02°; and the second set, focused on a specific region of the pattern, used a scanning rate of 1 min⁻¹ with steps of 0.02° in the 2θ range from 15 to 21°.

RESULTS AND DISCUSSION

Figure 1a presents IR ATR spectra of PTFE powder before and after planetary ball milling in the presence of sodium chloride, shown by the blue and red curves, respectively. In this spectral region, no peak related to sodium chloride appears,³² and all the peaks are attributed to PTFE. The native PTFE spectrum (blue) is characterized by two main peaks at about 1245 and 1146 cm⁻¹ that are assigned to the CF₂ antisymmetric (marked by #1) and symmetric stretching (marked by #2) vibration modes, respectively.²⁵

Another important two-band set is marked by #3, both of which are assigned to the CF_2 wagging vibration mode.²⁵ These two bands are known to be sensitive to the molecular conformation of PTFE, and the band intensity ratio is known to be useful as a quantitative marker of helix-reversal defects.^{24,33} The defect occurs where the helical twisting direction changes in the R_f chain.

The IR spectra show remarkable changes after milling in the presence of sodium chloride for all the bands. The band #1 shows a band "intensity" change at 1245 cm⁻¹, and the band #2 shows a minor but reproducible higher-wavenumber "shift" during milling from 1145.9 to 1150.3 cm⁻¹, as shown by the inset in the figure. On the other hand, the band set #3 shows a change in the band "intensity ratio". These three regions give us different information on the molecular changes that occurred in the PTFE crystal or within a single molecule, as follows.

#1 Fine Granulation of PTFE Revealed by Phonon Band. The most apparently significant change is found for the band #1. The band at 1245 cm⁻¹ looks newly in the spectrum after the milling process, while it is largely depressed in native PTFE. Fortunately, this band has already been studied in detail^{7,8,34} and is attributed to the surface mode of phonon,^{35,36} as a result of the strong intermolecular interaction between the large permanent dipole moments of the C–F bonds in the R_f group. In fact, Nagai and coworkers have shown that the electric permittivity in this band region drops down to a negative value, which means that the phonon becomes a polariton.^{9,10,37} This experimentally proves that the dipole– dipole coupling is extremely strong. Since the surface mode of phonon (or polariton) is localized at the surface of individual particles, the intensity of the surface mode is directly correlated to the relative surface area to volume. In other words, the significant increase of the surface-mode band straightforwardly indicates that PTFE is crushed into many fine particles having a large surface area. In this manner, IR spectroscopy proves that the particle size decreases as a result of the milling process.

#2 Disaggregation of PTFE Crystals. The band **#2** is of the CF₂ symmetric stretching vibration (ν_s (CF₂)) mode, which is often used as a marker band for "molecular aggregation" to discuss crystallinity or molecular packing, as mentioned elsewhere.³⁸ In the case of *n*-alkyl group having no fluorine, the corresponding CH₂ stretching vibration (ν_s (CH₂)) band is very sensitive to molecular conformation, which is directly influenced by molecular aggregation.^{22,23,39-46} In fact, the $\nu_{s}(CH_{2})$ band is often used as a marker band for molecular aggregation, and is sometimes used for discussing crystallinity. In the case of the $\nu_s(CF_2)$ band, this concept does not apply, since R_f groups are much stiffer than *n*-alkyl groups,^{1,12,47,48} meaning that conformational change is seriously suppressed. If this band is influenced solely by conformational changes, then the $\nu_s(CF_2)$ band should be insensitive to molecular aggregation.^{28,38} A largely different situation should be taken into account; however, in that the R_f molecules are strongly adhered to each other by dipole-dipole interactions, which can be ignored in the case of hydrocarbon chains. The strong aggregation of R_f groups makes the normal mode of a single molecule to change into a collective vibration, as found in phonon generation. As a result, the position of the $\nu_s(CF_2)$ band can be used as a marker of molecular aggregation or, in crystallinity.

As shown to the first decimal place in the inset of Figure 1a, the native PTFE shows a band at 1145.9 cm⁻¹ and it shifts to a higher wavenumber found at 1150.3 cm⁻¹. The shift of 4.4 cm⁻¹ is remarkably large for the R_f compounds,³⁸ suggesting a significant aggregational change, since such a large shift does not happen in a single molecule.

Then, the same sample was subjected to XRD analysis. As found in Figure 2a, the main diffraction peak of the (100) plane⁴⁹ found for the native PTFE (blue) is drastically



Figure 2. Main diffraction peaks of the (100) plane obtained by the powder XRD technique before (blue), after the ball-milling treatment with NaCl (red), and after milling without NaCl (black). (a) The peaks are plotted with the observed intensities, with error bars representing the standard error (SE) of the peak intensity. (b) The normalized peaks, with error bars representing the SE of the peak position. The average values of the full width at half-maximum (FWHM) of the individual peaks are also presented.



Figure 3. IR ATR spectra of PTFE powder before (blue) and after (black) the ball-milling treatment without adding NaCl.

depressed for the ball-milled sample in the presence of sodium chloride (red; with a very minute error bar). When the patterns are normalized (Figure 2b), the sodium chloride-treated sample shows a shift to a lower diffraction angle, meaning an increase in the distance between crystal planes, i.e., crystal expansion. In addition, the full width at half maximum (FWHM) is also larger, which indicates a decrease of crystal size, as indicated by the Scherrer equation.^{21,50} As predicted by the IR spectral changes, the crystallinity is found to be largely lost due to the milling process. As a result, molecular disaggregation is also confirmed in terms of crystallinity.

If sodium chloride is not added to the system, then what happens after the ball-milling process with the same milling conditions? The result is presented in Figure 3 by the black curve. Unlike the case where sodium chloride is used, as shown in Figure 1, no spectral change is found for both bands #1 and #2 in the higher wavenumber region (Figure 3a). This strongly indicates that only mechanical milling does not work on molecular disaggregation, and the addition of sodium chloride is key. As for the band #3, we have to note that the conformational defect still remains, which will be discussed later.

The same sample was analyzed by the XRD technique, as presented by the black curve in Figure 2. Although the peak intensity of the XRD has some variation, as presented by the error bars, we can say that the milled sample with sodium chloride is significantly different from the the rest samples, which supports that molecular disaggregation is driven by the addition of sodium chloride.

#3 Change of Molecular Conformation. The third important discussion point is found for the band #3 in the low-wavenumber IR region about 630 cm⁻¹ (Figure 1b). This band was first pointed out to be a marker of conformational change by Brown in 1964,²⁴ and, in particular, the band at 625 cm⁻¹ was supposed to be correlated with the "defect" occurring in an R_f chain. The defect means that the direction of twisting of the R_f group is interchanged, as schematically shown in Figure 4.

This schematic image was obtained as a conclusion of the temperature-dependent IR spectra in this wavenumber region.²⁴ At a very low temperature of about 100 K, nearly a single peak at 640 cm⁻¹ appeared, whereas a new peak at 625 cm⁻¹ developed at a higher temperature of about 300 K. Judging from the Stratified Dipole-Arrays (SDA) model,^{11,12,51} the molecular packing of R_f chains should have the lowest energy if the molecules have a common twisting direction throughout the chain because such a helical homogeneity theoretically contributes to a reasonable dipole–dipole interactive structure between molecules with a perpendicular stance.^{11,12,52,53} Since the most stable state is expected at a low temperature, the band at ca. 640 cm⁻¹ is thus considered to be



Figure 4. Schematic images of the defect-involved and -free R_f chains, as reflected in the IR spectra³³ in the region #3.

defect-free molecules. On the other hand, if the molecules are heated, the molecular packing can become slightly loose, creating an opportunity for defects to form in a molecule. As a matter of fact, Brown theorizes the ratio of defects to normal conformations as a function of temperature, and the theoretical ratio is consistent with experimental results.²⁴ In this manner, the band at 625 cm⁻¹ is assigned to defect-involving molecules. These experimental considerations are later proved by theoretical calculations on quantum mechanics,³³ and now we can discuss the spectra within this established concept.

Let us take a look at a magnified spectrum of region #3 in Figure 1b based on this concept. The band intensity ratio, I_{625}/I_{638} , of the milled PTFE with sodium chloride changes to be larger than the native PTFE ($0.86 \rightarrow 1.05$), which indicates that the number of defects is increased by milling with sodium chloride. If the molecules are in a highly packed crystal when milling is applied, such a conformational change is not expected because the molecular skeletons become more rigid due to aggregation. Therefore, the observed conformational change needs a decrease in crystallinity. In fact, as shown in Figure 2a, this conformational change is accompanied by a significant decrease in crystallinity. This process is schematically shown in Figure 5a-c.

Since the R_f chain is a collection of C-F bonds, having a large permanent dipole moment individually, the chain would readily be solvated by solvent molecules having a large dipole moment. In the present case, sodium chloride works for that, and the reaggregation of the PTFE is blocked by the solvation molecules. As a result, the molecules are kept disaggregated, having the defects as is (Figure 5d).

This is confirmed by using another additive having no permanent dipole moment, which is copper fine powder. The results are shown in Figure S2. Because copper is a metal, the IR spectrum is distorted a little. We find, however, that all the bands #1 through #3 regenerate the results with no additive

Article



Figure 5. Schematic showing the changes in molecular packing upon ball milling in the presence of sodium chloride. (a) Native PTFE. (b) After milling, the conformation is retained, and (c) conformational defects (marked by shaded color) are generated with a certain probability. (d) Sodium chloride works as a solvent to stabilize the disaggregated PTFE molecules, but (e) if not, the molecules are reaggregated. (f) If the sodium chloride on PTFE molecules is removed by water, the PTFE molecules are soon reaggregated.



Figure 6. IR ATR spectrum of the washed PTFE by water is shown by the green curve. The IR spectra of the PTFE powder measured before (blue) and after (red) the ball-milling treatment with NaCl are identical to those in Figure 1.

(Figure 3). Through this simple examination, the influence of the dipole moment (multipoles, indeed) is proved to be clear.

If the disaggregated molecules are not solvated, on the other hand, the molecules can be reaggregated to be back (Figure 5e). This schematic explains what is happening in Figure 3: no change is found for the bands #1 and #2, which indicates that the molecules are packed tightly as if they did not experience disaggregation at all (Figure 3a) while only the conformational change remains for the band #3 (reproducible) as a trace (Figure 3b). Since the conformational change requires room generated by disaggregation, the increase of defects suggests a history in which the matter was once disaggregated to some degree (Figure 5c) and then returned to the tightly packed state again (Figure 5e).

Finally, we are interested in the results when the solvated PTFE is washed out with water (Figure 5f) to fully remove sodium chloride from the molecular surface of PTFE. The spectrum of the water-washed sample is presented by the green curve in Figure 6.

As expected, the molecules are reaggregated to regenerate the IR bands #1 and #2, which are identical to those of the native PTFE. This further means that sodium chloride is readily removed by the water rinse. Of interest is the fact that the defects are kept unchanged after the water rinse, as found by the bands #3, meaning that the defects are not recovered during the reaggregation process.

CONCLUSION

IR spectroscopy is found to be a very powerful tool to discuss the molecular aggregation of PTFE by looking at three different wavenumber regions. These three regions reveal that: 1) the matter is crushed into small particles, as indicated by the phonon band intensity; 2) the particles are disaggregated to some extent; and 3) the disaggregated molecules can have conformational defects. If the molecules completely (or ideally) come apart into single molecules, no phonon bands would appear. Therefore, the appearance of the phonon band indicates that the matter is not disaggregated that much, but it is loosened to some degree. In this fashion, the ball-milling technique in the presence of sodium chloride is found to work well to loosen PTFE, which is expected to be a useful technique for reshaping the matter aimed at mechanical recycling.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcb.5c01148.

Figure S1, IR ATR spectra of high molecular-mass PTFE powder measured before (blue) and after (red) the crush with NaCl; Figure S2, IR ATR spectra of PTFE powder measured before (blue) and after (red) the crush in the presence of Cu fine powder (PDF)

AUTHOR INFORMATION

Corresponding Author

Takeshi Hasegawa – Laboratory of Chemistry for Functionalized Surfaces, Division of Environmental Chemistry, Institute for Chemical Research, Kyoto University, *Kyoto 611-0011, Japan;* orcid.org/0000-0001-5574-9869; Email: htakeshi@scl.kyoto-u.ac.jp

Authors

- **Tomoya Oonuki** Laboratory of Chemistry for Functionalized Surfaces, Division of Environmental Chemistry, Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan
- Taisuke Araki Laboratory of Chemistry for Functionalized Surfaces, Division of Environmental Chemistry, Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan
- Takayuki Oka Laboratory of Chemistry for Functionalized Surfaces, Division of Environmental Chemistry, Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan; ⊚ orcid.org/0009-0000-1677-4586
- Hiroshi Matsuda Laboratory of Chemistry for Functionalized Surfaces, Division of Environmental Chemistry, Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan
- Nobutaka Shioya Laboratory of Chemistry for Functionalized Surfaces, Division of Environmental Chemistry, Institute for Chemical Research, Kyoto University, Kyoto 611-0011, Japan; Orcid.org/0000-0002-2915-894X
- **Junya Kano** Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai 980-8577, Japan
- Akihide Hibara School of Science, Institute of Science Tokyo, Tokyo 152-8551, Japan; o orcid.org/0000-0003-0258-3361

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jpcb.5c01148

Author Contributions

The manuscript was written through contributions of all authors.

Funding

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Challenges in Research (Exploratory) (No. 21K18979 (TH)), a Grant-in-Aid for Scientific Research (B) (No. 22H02106 (TH)), and a Grant-in-Aid for Early-Career Scientists (No. 22K14604 (NS)) from the Japan Society for the Promotion of Science (JSPS), and the Asahi Glass Foundation (TH), to which the authors' thanks are due. The calculated spectrum in Figure 4 was obtained by us using Gaussian16 C.01⁵⁴ running on the supercomputer of ACCMS, Kyoto University, and was found to agree with the reference #33.

REFERENCES

(1) Krafft, M. P.; Riess, J. G. Chemistry, Physical Chemistry, and Uses of Molecular Fluorocarbon–Hydrocarbon Diblocks, Triblocks, and Related Compounds-Unique "Apolar" Components for Self-Assembled Colloid and Interface Engineering. *Chem. Rev.* **2009**, *109* (5), 1714–1792.

(2) Perfluoroalkyl Substances: Synthesis, Applications, Challenges and Regulations; Ameduri, B.; RSC: London, UK, 2022.

(3) Krafft, M. P.; Riess, J. G. Selected Physicochemical Aspects of Poly- and Perfluoroalkylated Substances Relevant to Performance, Environment and Sustainability—Part One. *Chemosphere* **2015**, *129*, 4–19.

(4) Krafft, M.P; Riess, J.G Highly Fluorinated Amphiphiles and Colloidal Systems, and Their Applications in the Biomedical Field. A Contribution. *Biochimie* **1998**, *80*, 489–514.

(5) Plunkett, R. J. The History of Polytetrafluoroethylene: Discovery and Development. In High Performance Polymers: Their Origin and Development, In *High Performance Polymers: Their Origin and Development.*, Seymour, R. B.; Kirshenbaum, G. S. Eds; Springer, Dordrecht, 1986, pp. 261–266.

(6) Hasegawa, T. Understanding of the Intrinsic Difference between Normal- and Perfluoro-Alkyl Compounds toward Total Understanding of Material Properties. *Chem. Phys. Lett.* **2015**, *627*, *64*–*66*.

(7) Hasegawa, T.; Nakagawara, A.; Takagi, T.; Shimoaka, T.; Shioya, N.; Sonoyama, M. Phonon Modes Controlled by Primary Chemical Structure of Partially Fluorinated Dimyristoylphosphatidylcholine (DMPC) Revealed by Multiple-Angle Incidence Resolution Spectrometry (MAIRS). J. Chem. Phys. 2024, 160 (6), 064704.

(8) Fukumi, A.; Shimoaka, T.; Shioya, N.; Nagai, N.; Hasegawa, T. Infrared Active Surface Modes Found in Thin Films of Perfluoroalkanes Reveal the Dipole–Dipole Interaction and Surface Morphology. J. Chem. Phys. **2020**, 153 (4), 044703.

(9) Nagai, N.; Okada, H.; Hasegawa, T. Morphology-Sensitive Infrared Absorption Bands of Polymers Derived from Surface Polaritons. *AIP Adv.* **2019**, *9* (10), 105203.

(10) Amaki, Y.; Okada, H.; Nagai, N. Structural Analysis of Injection-Molded Polyoxymethylene Treated Below a Melting Point Using Field-Emission Scanning Electron Microscopy and Infrared Spectroscopy. *Appl. Spectrosc.* **2022**, *76* (6), 699–711.

(11) Hasegawa, T.; Shimoaka, T.; Shioya, N.; Morita, K.; Sonoyama, M.; Takagi, T.; Kanamori, T. Stratified Dipole-Arrays Model Accounting for Bulk Properties Specific to Perfluoroalkyl Compounds. *ChemPluschem* **2014**, *79* (10), 1421–1425.

(12) Hasegawa, T. Physicochemical Nature of Perfluoroalkyl Compounds Induced by Fluorine. *Chem. Rec.* 2017, 17 (10), 903–917.

(13) Mauritz, K. A.; Moore, R. B. State of Understanding of Nafion. *Chem. Rev.* **2004**, *104* (10), 4535–4586.

(14) Iwamoto, R.; Oguro, K.; Sato, M.; Iseki, Y. Water in Perfluorinated Sulfonic Acid Nafion Membranes. J. Phys. Chem. B 2002, 106 (28), 6973–6979.

(15) Wakai, C.; Shimoaka, T.; Hasegawa, T. Characterization of Adsorbed Molecular Water on the Surface of a Stretched Polytetrafluoroethylene Tape Analyzed by ¹H NMR. *J. Phys. Chem.* B **2016**, *120* (9), 2538–2543.

(16) Wakai, C.; Shimoaka, T.; Hasegawa, T. 1H NMR Analysis of Water Freezing in Nanospace Involved in a Nafion Membrane. J. Phys. Chem. B 2015, 119 (25), 8048–8053.

(17) Shimoaka, T.; Wakai, C.; Sakabe, T.; Yamazaki, S.; Hasegawa, T. Hydration Structure of Strongly Bound Water on the Sulfonic Acid Group in a Nafion Membrane Studied by Infrared Spectroscopy and Quantum Chemical Calculation. *Phys. Chem. Chem. Phys.* **2015**, *17* (14), 8843–8849.

(18) Han, S.; Wang, Y.; Xu, Y.; Wu, J. Preparation of Foam Material via Co-Sintering of NaCl and PTFE for Oil/Water Separation. *J. Porous Mater.* **2024**, *31* (3), 1005–1014.

(19) Leung, S. C. E.; Wanninayake, D.; Chen, D.; Nguyen, N.-T.; Li, Q. Physicochemical Properties and Interactions of Perfluoroalkyl Substances (PFAS) - Challenges and Opportunities in Sensing and Remediation. *Sci. Total Environ.* **2023**, *905*, 166764.

(20) Vert, M.; Doi, Y.; Hellwich, K.-H.; Hess, M.; Hodge, P.; Kubisa, P.; Rinaudo, M.; Schué, F. Terminology for Biorelated Polymers and Applications (IUPAC Recommendations 2012). *Pure Appl. Chem.* **2012**, *84* (2), 377–410.

(21) Nishimura, S.; Li, Y.; Semba, Y.; Hibara, A.; Oonuki, T.; Hasegawa, T.; Kano, J. Mechanochemical Processing of Polytetrafluoroethylene with NaCl Crystal. Bullet Chemical Social Japan. 2025, in press.

(22) Hasegawa, T. Quantitative Infrared Spectroscopy for Understanding of a Condensed Matter; Springer Tokyo, 2017.

(23) Tolstoy, V. P.; Chernyshova, I. V.; Skryshevsky, V. A. Handbook of Infrared Spectroscopy of Ultrathin Films; John Wiley & Sons, Inc., 2003. DOI: .

(24) Brown, R. Vibrational Spectra of Polytetrafluoroethylene: Effects of Temperature and Pressure. J. Chem. Phys. **1964**, 40 (10), 2900–2908.

(25) Hannon, M.; Boerio, F.; Koenig, J. Vibrational Analysis of Polytetrafluoroethylene. J. Chem. Phys. **1969**, 50 (7), 2829–2836.

(26) Boerio, F. J.; Koenig, J. L. Vibrational Spectroscopy of Polymers. J. Macromol. Sci. Part C 1972, 7 (2), 209–249.

(27) Cho, H. G.; Strauss, H. L.; Snyder, R. G. Infrared Spectra and Structure of Perfluoro-n-Alkanes Isolated in n-Alkane Matrixes Prepared by Vapor Deposition. *J. Phys. Chem.* **1992**, *96* (13), 5290–5295.

(28) Araki, T.; Oka, T.; Shioya, N.; Hasegawa, T. Molecular Symmetry Change of Perfluoro-n-Alkanes in 'Phase I' Monitored by Infrared Spectroscopy. *Anal. Sci.* **2024**, *40*, 1723–1731.

(29) Cruz, R.; Ataka, K.; Heberle, J.; Kozuch, J. Evaluating Aliphatic CF, CF2, and CF3 Groups as Vibrational Stark Effect Reporters. *J. Chem. Phys.* **2024**, *160* (20), 204308.

(30) Steiner, P. A.; Gordy, W. Precision Measurement of Dipole Moments and Other Spectral Constants of Normal and Deuterated Methyl Fluoride and Methyl Cyanide. *J. Mol. Spectrosc.* **1966**, *21* (1–4), 291–301.

(31) Griffiths, P. R.; de Haseth, J. A. Fourier Transform Infrared Spectroscopy; Wiley Interscience, 2007.

(32) Kittel, C. Introduction To Solid State Physics (8th Ed.); John Wiley & Sons, Inc., 2005.

(33) Quarti, C.; Milani, A.; Castiglioni, C. Ab Initio Calculation of the IR Spectrum of PTFE: Helical Symmetry and Defects. *J. Phys. Chem. B* 2013, *117* (2), 706–718.

(34) Nagai, N.; Okawara, M.; Kijima, Y. Infrared Response of Sub-Micron-Scale Structures of Polyoxymethylene: Surface Polaritons in Polymers. *Appl. Spectrosc.* **2016**, *70* (8), 1278–1291.

(35) Ruppin, R.; Englman, R. Optical Phonons of Small Crystals. Rep. Prog. Phys. 1970, 33 (1), 149.

(36) Ruppin, R. Surface Effects on Optical Phonons and on Phonon-Plasmon Modes. *Surf. Sci.* **1973**, *34* (1), 20–32.

(37) Nakajima, S.; Toyozawa, Y.; Abe, R. The Physics of Elementary Excitations; Springer, 2080.

(38) Kise, R.; Fukumi, A.; Shioya, N.; Shimoaka, T.; Sonoyama, M.; Amii, H.; Takagi, T.; Kanamori, T.; Eda, K.; Hasegawa, T. Fluorous Property of a Short Perfluoroalkyl-Containing Compound Realized by Self-Assembled Monolayer Technique on a Silicon Substrate. *Bull. Chem. Soc. Jpn.* **2019**, 92 (4), 785–789.

(39) Hasegawa, T.; Takeda, S.; Kawaguchi, A.; Umemura, J. Quantitative Analysis of Uniaxial Molecular Orientation in Langmuir-Blodgett Films by Infrared Reflection Spectroscopy. *Langmuir* **1995**, *11* (4), 1236–1243.

(40) Umemura, J.; Takeda, S.; Hasegawa, T.; Kamata, T.; Takenaka, T. Effect of Thickness and Monolayer Location on Thermostability of Metal Stearate LB Films Studied by FT-IR Reflection—Absorption Spectroscopy. *Spectrochim. Acta Part A: Mol. Spectrosc.* **1994**, *50* (8–9), 1563–1571.

(41) Umemura, J.; Hasegawa, T.; Sakai, H.; Takenaka, T. FT-IR External Reflection Spectra of L and LB Films. *Trans. Mater. Res. Jpn.* **1994**, *15A*, 583–586.

(42) Umemura, J.; Takeda, S.; Hasegawa, T.; Takenaka, T. Thickness and Temperature Dependence of Molecular Structure in Stearic Acid LB Films Studied by FT-IR Reflection—Absorption Spectroscopy. J. Mol. Struct. **1993**, 297, 57–62.

(43) Hasegawa, T.; Umemura, J.; Takenaka, T. Fourier Transform Infrared Metal Overlayer Attenuated Total Reflection Spectra of Langmuir-Blodgett Films of 12-Hydroxystearic Acid and Its Cadmium Salt. *Thin Solid Films* **1992**, *210*, 583–585. (44) Hasegawa, T.; Kamata, T.; Umemura, J.; Takenaka, T. Thermal Stability of Metal Stearate LB Films Studied by Infrared Reflection– Absorption Spectroscopy. *Chem. Lett.* **1990**, *19* (9), 1543–1546.

(45) Shioya, N.; Yoshida, M.; Fujii, M.; Eda, K.; Hasegawa, T. Disappearance of Odd-Even Effects at the Substrate Interface of N-Alkanes. J. Am. Chem. Soc. **2024**, 146 (46), 32032-32039.

(46) Shioya, N.; Yoshida, M.; Fujii, M.; Shimoaka, T.; Miura, R.; Maruyama, S.; Hasegawa, T. Conformational Change of Alkyl Chains at Phase Transitions in Thin Films of an Asymmetric Benzothienothiophene Derivative. *J. Phys. Chem. Lett.* **2022**, *13* (51), 11918– 11924.

(47) Bunn, C. W. The Melting Points of Chain Polymers. J. Polym. Sci., Part B: polym. Phys. **1996**, 34 (5), 799–819.

(48) Bunn, C. W.; Cobbold, A. J.; Palmer, R. P. The Fine Structure of Polytetrafluoroethylene. J. Polym. Sci. **1958**, 28 (117), 365–376.

(49) Li, S. T.; Arenholz, E.; Heitz, J.; Bäuerle, D. Pulsed-Laser Deposition of Crystalline Teflon (PTFE) Films. *Appl. Surf. Sci.* **1998**, 125 (1), 17–22.

(50) Als-Nielsen, J.; McMorrow, D. Elements of Modern X-ray Physics; Wiley, 2011.

(51) Shimoaka, T.; Sonoyama, M.; Amii, H.; Takagi, T.; Kanamori, T.; Hasegawa, T. Raman Optical Activity on a Solid Sample: Identification of Atropisomers of Perfluoroalkyl Chains Having a Helical Conformation and No Chiral Center. *J. Phys. Chem. A* **2019**, *123* (18), 3985–3991.

(52) Hasegawa, T.; Shimoaka, T.; Tanaka, Y.; Shioya, N.; Morita, K.; Sonoyama, M.; Amii, H.; Takagi, T.; Kanamori, T. An Origin of Complicated Infrared Spectra of Perfluoroalkyl Compounds Involving a Normal Alkyl Group. *Chem. Lett.* **2015**, *44* (6), 834–836.

(53) Honda, K.; Morita, M.; Otsuka, H.; Takahara, A. Molecular Aggregation Structure and Surface Properties of Poly(Fluoroalkyl Acrylate) Thin Films. *Macromolecules* **2005**, *38* (13), 5699–5705.

(54) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H., et al. *Gaussian 16, Revision C.01*; Gaussian, Inc.: Wallingford, CT, 2019.