Macromolecules

ARTICLE

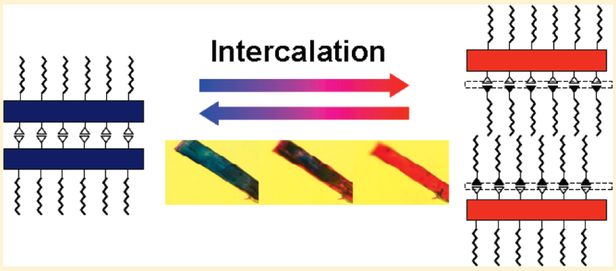
pubs.acs.org/Macromolecules

Structural and Chromatic Changes of Host Polydiacetylene Crystals during Intercalation with Guest Alkylamines

Tomoyo Shimogaki and Akikazu Matsumoto*

Department of Applied Chemistry and Bioengineering, Graduate School of Engineering, Osaka City University, 3-3-138, Sugimoto, Sumiyoshi-ku, Osaka 558-8585, Japan

S *Supporting Information*



ABSTRACT: We report a new type of intercalation system using the host polydiacetylene (PDA) crystals including a carboxylic acid in the side chain in combination with various guest alkylamines. The role of the phenylene or methylene spacer between the conjugated main chain and the carboxylic acid on the intercalation property was investigated using three kinds of PDAs, i.e., poly(1,3-hexadecadiynyl-4-benzoic acid), poly(2,4-heptadecadiynoic acid), and poly(10,12-pentacosadiynoic acid), as the host polymer crystals. The color of the PDA crystals changed from blue to red by the addition of the amines. A change in the interlayer distance of the host polymer crystals according to the size of the guest amines was determined, and the inclined structure of the alkyl groups was discussed based on the powder X-ray diffraction data. We further succeeded in the direct observation of the intercalation reaction process by monitoring the color change in a large PDA crystal using optical microscopy.

■ INTRODUCTION

Many kinds of conjugated polymers have been designed and synthesized due to their eminent properties,[1] such as use in organic light-emitting diodes,[2] third-order nonlinear optical properties,[3] and chemical or biochemical sensing.[4] Polydiacetylenes (PDAs) as one of the conjugated polymers have been investigated as the key materials changing their intrinsic blue-to-red color and fluorescence properties in response to external stimuli or environmental perturbations.[5−7] The repeated color change of PDAs is expected to be used for various applications, but in most of the actual cases, their chromatic transition reversibly occurs under limited conditions. For example, poly(10,12-pentacosadiynoic acid) [poly(*12,8*-DA-CO_2H)] exhibited a partially reversible color change between the initial blue and the intermediate purple in the temperature range below 50 °C, followed by an irreversible change to the final red one upon further heating.[8] When any strong interaction is introduced into the side chain of the PDAs, the PDAs exhibit a reversible color change over a wider temperature range.[9] Recently, we investigated the molecular packing structure and the solid-state polymerization behavior of diacetylene compounds containing a naphthylmethylammonium carboxylate in the side chain.[10] The PDAs with robust two-dimensional (2D) hydrogen bond networks directly bound to the main chain exhibited a reversible color change over a wide temperature range upon heating.

We previously reported an intercalation system using organic layered host materials, which were obtained by the topochemical polymerization of alkylammonium muconates and sorbates.[11−14] For example, the ammonium muconate polymer crystals are converted into poly(muconic acid) (PMA) crystals by hydrolysis with HCl in an aqueous methanol or by thermolysis in the solid state, and the process is reversible. Some alkylamine molecules as the guests are intercalated into the PMA crystals dispersed in a methanol solution of the amine with stirring at room temperature. During the intercalation and its reverse reaction (i.e., deintercalation), the guest amines are inserted into the polymer crystals and reversibly removed from them. The transformation heterogeneously occurs because both the polymer crystals as the acid and the ammonium salts are insoluble in methanol as the dispersant. Nevertheless, intercalation proceeds with a high efficiency to achieve a high conversion. The PDAs are also one of the promising candidates as the polymer host compound for organic intercalation because they have a lamellar structure similar to the polymers obtained from 1,3-diene monomers.[15]

In the present study, we synthesized three kinds of PDAs containing a carboxylic acid in the side chain with or without a phenylene or methylene spacer between the main chain and the carboxylic acid, i.e., poly(1,3-hexadecadiynyl-4-benzoic acid) [poly(*12,Ph*-DA-CO_2H)], poly(2,4-heptadecadiynoic acid) [poly(*12,0*-DA-CO_2H)], and poly(*12,8*-DA-CO_2H), as shown in Figure 1. We investigated the intercalation behavior of the PDAs as the host polymers using various amines as the guests and the structural changes of the layered polymer crystals during the intercalation. We also succeeded in the visualization of an intercalation reaction using large-size PDA crystals.

Received: February 1, 2011
Revised: March 15, 2011
Published: April 05, 2011

■ EXPERIMENTAL SECTION

General Procedure. The NMR spectra were recorded using a JEOL JMN A400 spectrometer or a Bruker AV300 spectrometer in CD_3OD, $CDCl_3$, or DMSO-d_6 as the solvents. The FT-IR spectra were recorded using a JASCO FT/IR 430 spectrometer equipped with a JASCO Intron IRT-30 infrared microscope. The wide-angle X-ray diffraction data were collected using a Rigaku X-ray diffractometer RINT-Ultima 2100 with Cu Kα radiation (λ = 1.5418 Å). The UV–vis spectra were recorded using a JASCO V-550 spectrophotometer at ambient temperature for the PDA dispersions. The intercalation behavior of the large-size PDA crystals was directly monitored using a Nikon ECLIPSE E600 POL optical microscope equipped with a Hamamatsu PMA-11 detector.

Preparation of PDAs. The *12,Ph*-DA-CO_2H and *12,0*-DA-CO_2H were prepared by the Cadiot–Chodkiewicz coupling reaction.[16] The photopolymerization of *12,Ph*-DA-CO_2H was carried out in the solid state under γ-radiation, which was carried out at a radiation dose of 200 or 1000 kGy (a dose rate of 9.7 kGy/h) and 400 kGy (a dose rate of 16.7 kGy/h) using ^{60}Co at an Osaka Prefecture University facility. The blue or bluish green poly(*12,Ph*-DA-CO_2H) was isolated as the insoluble part in methanol, and the polymer yield was gravimetrically determined. Poly(*12,0*-DA-CO_2H) was prepared by the solid-state polymerization with a low-pressure mercury lamp (As-One SLUV-4, 9 W, 254 nm) at a distance of 5 cm. The resulting poly(*12,0*-DA-CO_2H) was filtered, washed with methanol, and then dried. The poly(*12,0*-DA-CO_2H) was isolated as a purple metallic solid. Commercially available *12,8*-DA-CO_2H (Alfa) was polymerized in the solid state under UV irradiation with a high-pressure mercury lamp (Toshiba SHL-100-2, 100 W) or a low-pressure mercury lamp (As-One SLUV-4, 9 W, 254 nm) at a distance of 10 or 5 cm, respectively. The resulting polymers were stirred in methanol, filtered, and then dried. Poly(*12,8*-DA-CO_2H) was isolated as a purple powdery solid.

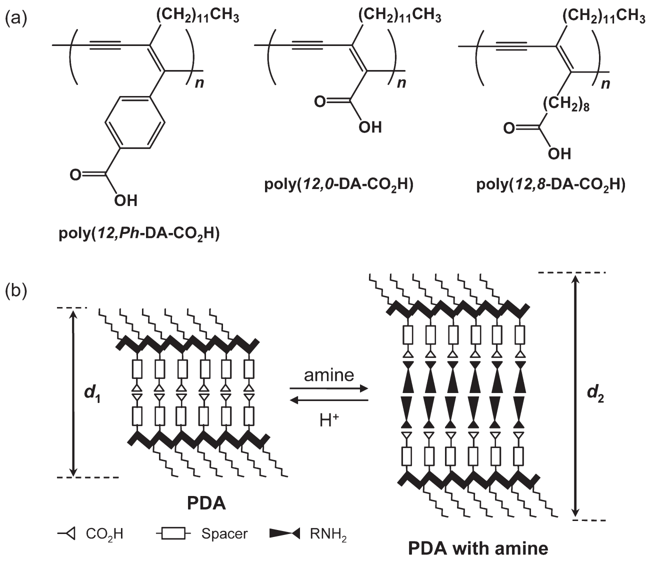


Figure 1. (a) PDAs containing a carboxylic acid in the side chain used as the host materials for intercalation. (b) Schematic illustration for a structural change expected during the intercalation of a guest amine to the host PDA.

Intercalation and Deintercalation Reactions. A typical procedure for the intercalation is as follows. The PDA powder (fine crystals) or large-size crystals, typically 20 mg, were dispersed in a solution (15 mL) of the desired amount of amine and stirred at room temperature. The polymer crystals were isolated with a filter, washed with a small amount of fresh solvent, and dried in vacuo. The conversion was determined by a gravimetric method or a change in the peak intensity in the IR spectrum using the intensity of the peak observed at 1469 cm^{-1} as the internal standard. The deintercalation of the crystals intercalated with an amine (i.e., ammonium crystals) was carried out by the addition of a concentrated HCl aqueous solution. A color change during the reactions was monitored using an optical microscope.

■ RESULTS AND DISCUSSION

Intercalation Behavior. We investigated the intercalation using three types of PDAs and various alkylamines with a different alkyl chain length as the host and guest, respectively. The conversion of the acid to the ammonium was determined by an increase in the polymer weight or an increase in the peak intensity of the absorption band due to the ammonium carboxylate and a decrease in that of the carboxylic acid in the IR spectrum. Figure 2 shows the time–conversion relationships for the intercalation using various guest alkylamines under the equimolar conditions for an amine concentration versus the carboxylic acid. The intercalation of the octadecylamine readily proceeded and achieved a high and constant conversion to the corresponding ammonium polymers when the poly(*12,Ph*-DA-CO_2H) was used as the host. The conversion was dependent on the carbon number of the guest alkylamines but independent of the reaction time. The greater the carbon number of the alkylamine, the higher the conversion. The color of the polymer was immediately changed from an original blue or purple to red when the amine was added. This indicates the rapid intercalation reaction process. Poly(*12,0*-DA-CO_2H) showed a reaction behavior similar to that of poly(*12,Ph*-DA-CO_2H). The average

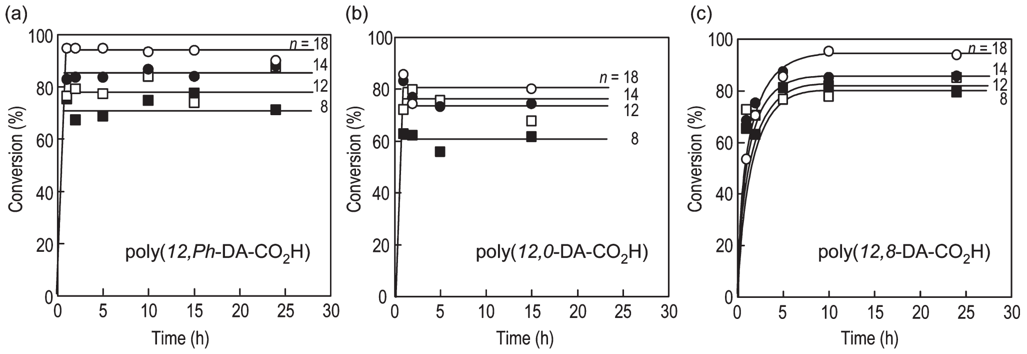


Figure 2. Time–conversion relationships for the intercalation using (a) poly(*12,Ph*-DA-CO_2H), (b) poly(*12,0*-DA-CO_2H), and (c) poly(*12,8*,DA-CO_2H) as the host in methanol. Guest: (■) octylamine, (□) dodecylamine, (●) tetradecylamine, and (○) octadecylamine. $[-NH_2]/[-CO_2H] = 1$.

Table 1. Maximum Conversion for the Intercalation Using Various PDA Host and Guest Alkylamines with Different Carbon Lengths

	conversion (%)		
carbon length of alkylamine	poly(*12,Ph*-DA-CO_2H)	poly(*12,0*-DA-CO_2H)	poly(*12,8*-DA-CO_2H)
8	71.7 ± 5.8	60.5 ± 7.0	80.7 ± 9.6
12	79.1 ± 5.7	74.6 ± 6.2	81.4 ± 9.9
14	84.5 ± 5.5	76.9 ± 5.0	85.3 ± 4.4
18	93.9 ± 1.8	80.0 ± 10.4	94.5 ± 3.6

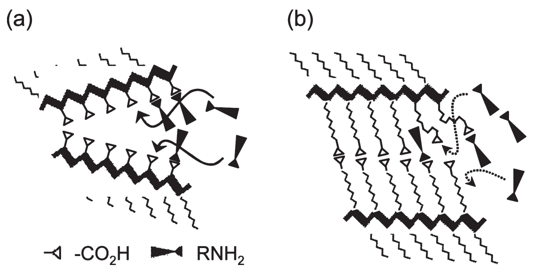


Figure 3. Schematic illustration for intercalation behavior using (a) poly(*12,Ph*-DA-CO_2H) or poly(*12,0*-DA-CO_2H) and (b) poly(*12,8*-DA-CO_2H) as the host.

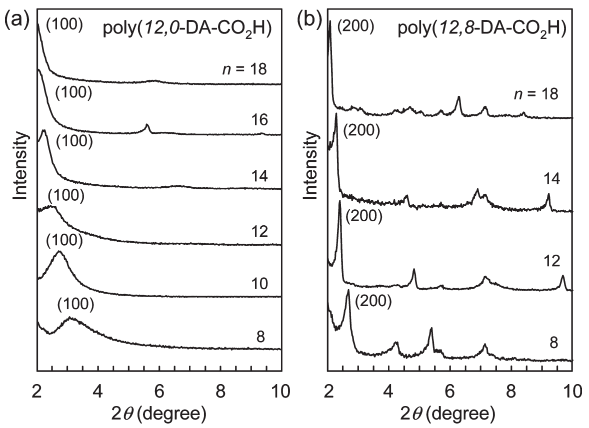


Figure 4. XRD profiles for (a) poly(*12,0*-DA-CO_2H) and (b) poly(*12,8*-DA-CO_2H) intercalated with alkylamines. $[-NH_2]/[-CO_2H] = 1$; the reaction time, 24 h. *n* is the carbon number of the used alkylamines.

conversions were slightly lower than those for the intercalation using poly(*12,Ph*-DA-CO_2H) (Figure 2 and Table 1). In contrast, the intercalation using poly(*12,8*-DA-CO_2H) slowly proceeded, and a color change was confirmed after stirring for several hours. The maximum conversions achieved 81−95% after a 24 h reaction, similar to those for the reaction with poly(*12,Ph*-DA-CO_2H). A difference in the initial reaction rates is due to the presence or absence of a flexible alkyl chain between the main chain and the carboxy group. Poly(*12,0*-DA-CO_2H) and poly(*12,Ph*-DA-CO_2H) have a carboxylic acid, which can conjugate to the main chain, whereas poly(*12,8*-DA-CO_2H) involves an octamethylene spacer between the main chain and the carboxy group. The schematic illustration of the intercalation reactions is shown in Figure 3. When the carboxylic acid is located near the main chain, the insertion of some guest amine molecules expands the interlayer space, which can further accelerate the insertion of guest amine molecules. On the other hand, no cooperating effect of the guest insertion is expected during the initial stage of the intercalation using the poly(*12,8*-DA-CO_2H) host due to the presence of a flexible methylene spacer. The rearrangement of the flexible side alkyl chains of the host polymer and the guest amines finally resulted in a complete intercalated structure at the high conversions.

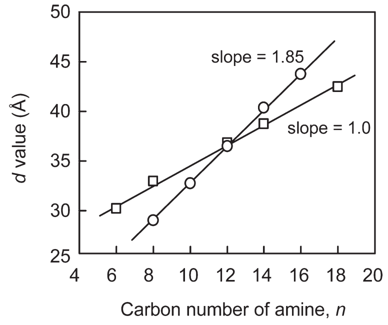


Figure 5. Plots of the *d* value versus the carbon number of alkylamines for (○) poly(*12,0*-DA-CO_2H) and (□) poly(*12,8*-DA-CO_2H) as the host.

Layer Structure of the Intercalated PDAs. The XRD measurement was carried out in order to investigate the layer structures of the poly(*12,0*-DA-CO_2H) and poly(*12,8*-DA-CO_2H) intercalated with various alkylamines (Figure 4). The characteristic diffractions were observed in a small angle region ($2\theta = 2°-3°$). The diffraction lines are assigned to the (100) and (200) planes for poly(*12,0*-DA-CO_2H) and poly(*12,8*-DA-CO_2H), respectively. The interlayer distances depended on the length of the guest amines, as shown in Figure 5. The *d*-value linearly increased as the function of the alkyl carbon number (*n*) of the used amines, and the slope of the line was 1.85 and 1.0 Å for the intercalations using poly(*12,0*-DA-CO_2H) and poly(*12,8*-DA-CO_2H), respectively.[10] This result indicated that the guest alkylamines are intercalated with 43° and 38° inclined angles against the polymer sheet. The latter value was similar to that for the previously reported PMA.[13,14] The angle 38° is the best fit to the alkyl chain stacking with a lattice of 4.5 and 7.4 Å lengths, which is a typical unit cell structure for *n*-alkanes and polyethylene.[17] For poly(*12,0*-DA-CO_2H) with no spacer, the guest amines incline at a larger angle to the polymer sheet. It was previously revealed that the corresponding monomer molecules were packed with a double-layer structure because a carboxy group formed dimer and a side alkyl chain inclined at 44° to the polymer sheet in the crystals.[10] Similar inclined angles were also reported for the other systems, such as organic−inorganic layer composites.[18] These results indicate that the distance between the PDA chains in the sheets is longer than that for PMA and that

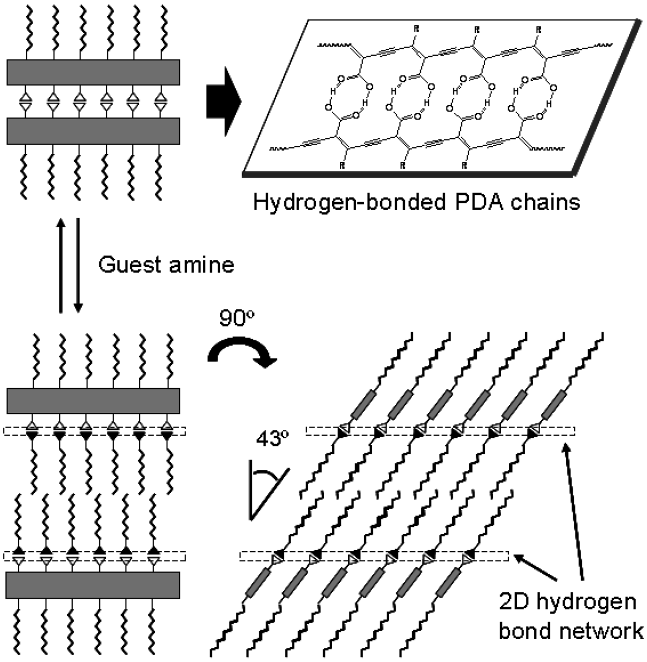


Figure 6. Schematic illustration of the host poly(*12,0*-DA-CO_2H) and the polymer intercalated with an alkylamine.

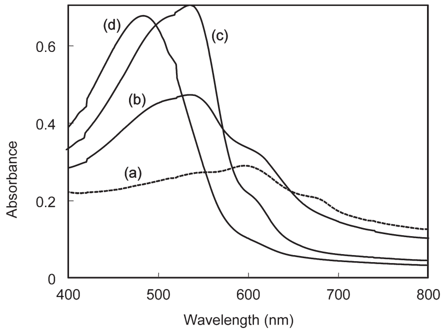


Figure 7. UV−vis absorption spectra of (a) poly(*12,Ph*-DA-CO_2H) and after intercalation with (b) octadecylamine, (c) *tert*-butylamine, and (d) 3-methoxypropylamine.

the packing structure of the guest amines changes depended on the presence or absence of an alkyl spacer between the main chain and carboxylic acid of the host PDAs.

In the case of poly(*12,8*-DA-CO_2H) with an alkyl spacer, the ammonium polymer crystals have 2D hydrogen-bond networks similar to that of PMA,[19] in which the guest amines are intercalated between the polymer sheets with a 38° inclined angle. The polymer crystals are expanded along the direction perpendicular to the plane of the 2D hydrogen-bond networks.[10] On the other hand, the carboxy groups of poly(*12,0*-DA-CO_2H) exist in the layer of the polymer conjugating plane. As a result, the ammonium polymers produced by the intercalation using poly(*12,0*-DA-CO_2H) include a different network structure. The guest amines form a packing structure with the side alkyl chain and inclined with the same angle as the side alkyl chain, as shown in Figure 6.

Visualization of Intercalation. Figure 7 shows the changes in the UV−vis absorption spectra during the intercalation using poly(*12,Ph*-DA-CO_2H) as the host and various alkylamines as the guest in a chloroform dispersion. When an amine as the guest was added to the PDA dispersed solution, the dispersed solution changed from blue or purple to red. In the literature,[7] many experimental approaches and discussions on the chromatic change of the PDA have been reported, but a mechanism for the color change is not fully clarified yet. The color change of PDA is induced by a change in the polymer backbone structure and the intermolecular interaction between the π-conjugated systems as well as conformational changes in the side chain and the mechanical strains of the conjugated main chains. We are now trying to determine the change in the single crystal structures of the PDAs during the thermochromism. In this study, when the amine was added to the PDA dispersion, the intensity of the absorption band at 550 nm increased independent of the guest alkyl chain length. Similarly, the intensity of the peak at 500−550 nm increased after the intercalation using not only alkylamines but also amines, implying a polar group. The absorption peak shifted to 480 nm, and its intensity became weaker in the case using an amine with a bulky substituent, such as *tert*-butylamine. We also tested the intercalation of secondary amines, but the spectrum change was small due to a low conversion. Oshita et al.[13] reported that the secondary and tertiary amines were hardly intercalated into the PMA due to the formation of hydrogen bond networks different from those formed with a primary amine.

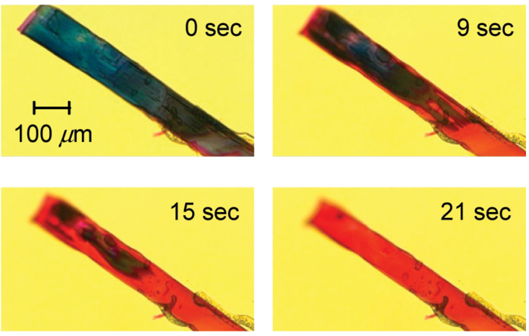


Figure 8. Optical microscopic observation of the intercalation of 1-cyclohexylethylamine into the poly(*12,Ph*-DA-CO_2H) crystal dispersed in ethanol. The amine was added to ethanol as the dispersant at the right and bottom position in the image. The movies are available as Supporting Information.

We further succeeded in the *in situ* observation of the intercalation reactions by the color change in the PDA crystals. Figure 8 shows the optical microscopic images of the poly(*12,Ph*-DA-CO_2H) during the intercalation using 1-cyclohexylethylamine as the guest. The blue-to-red color change gradually occurred from a position in which the amine molecules diffuse into the crystal and form the ammonium carboxylate polymer. Because the guest amines were favorably intercalated along the direction parallel to the polymer chain, the migration rate of the front line of the reaction was faster in the direction along the polymer chain. We also attempted deintercalation to investigate the reversibility of the color change. The deintercalation reaction was caused by the addition of a concentrated HCl solution. During the deintercalation reaction of a PDA crystal, the color change indicates the reversible intercalation of the PDAs. The results of the intercalation and deintercalation using the three PDAs are summarized in Table 2. For the PDAs with a rigid main-chain structure, poly(*12,Ph*-DA-CO_2H) and poly(*12,0*-DA-CO_2H), the color change was reversible. The reversibility of the color change is related to the

Table 2. Change in the Color of the Polymers and the Reversibility of Reactions during Intercalation and Deintercalation Processes Using PDA

PDA	original color of PDA	after intercalation	after deintercalation	reversibility
poly(*12,Ph*-DA-CO$_2$H)	blue	red	bluish purple	reversible
poly(*12,0*-DA-CO$_2$H)	bluish purple	red	bluish purple	reversible
poly(*12,8*-DA-CO$_2$H)	bluish purple	red	red	irreversible

thermochromism of the 1-naphthylmethylammonium carboxylate of these polymers in a previous paper.[10b]

CONCLUSIONS

We investigated the intercalation behavior using three types of PDAs as the host polymer material. The interlayer distance depended on the length of the guest amines, but the alignment of the guest is dependent on the host PDA structure. The color of the PDA dispersion changed from blue to red by the addition of an amine during the intercalations. Using the color change of a large PDA crystal, we succeeded in observing the intercalation behavior.

ASSOCIATED CONTENT

Ⓢ Supporting Information. Movies for intercalation and deintercalation. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail: matsumoto@a-chem.eng.osaka-cu.ac.jp.

ACKNOWLEDGMENT

This work was partially supported by Grant-in-Aids from the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST) and for Scientific Research from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

REFERENCES

(1) (a) Skothem, T. A., Reynolds, J. R., Eds.; *Handbook of Conjugating Polymers*, 3rd ed.; CRC Press: New York, 2007. (b) Leclerc, M., Morin, J.-F., Eds.; *Design and Synthesis of Conjugated Polymers*; Wiley-VCH: Weinheim, 2010. (c) Chujo, Y., Ed.; *Conjugated Polymer Synthesis*; Wiley-VCH: Weinheim, 2010.

(2) (a) Kraft, A.; Grimsdale, A. C.; Holmes, A. B. *Angew. Chem., Int. Ed.* **1998**, *37*, 402. (b) McCullough, R. D. *Adv. Mater.* **1998**, *10*, 93. (c) Martin, R. E.; Diederich, F. *Angew. Chem., Int. Ed.* **1999**, *38*, 1350. (d) Bunz, U. H. F. *Chem. Rev.* **2000**, *100*, 1605. (e) Dimitrakopoulos, C. D.; Malenfant, P. R. L. *Adv. Mater.* **2002**, *14*, 99. (f) Scherf, U.; List, E. J. W. *Adv. Mater.* **2002**, *14*, 477. (e) Yokozawa, T. *Macromolecules* **2007**, *40*, 4093. (f) Morisaki, Y.; Chujo, Y. *Angew. Chem., Int. Ed.* **2006**, *45*, 2.

(3) (a) Chemla, D. S., Zyss, J., Eds.; *Nonlinear Optical Properties of Organic Molecules and Crystals*; Academic Press: New York, 1987. (b) Sarkar, A.; Okada, S.; Matsuzawa, H.; Matsuda, H.; Nakanishi, H. *J. Mater. Chem.* **2000**, *10*, 819.

(4) (a) Swager, T. M. *Acc. Chem. Res.* **1998**, *31*, 201. (b) Thomas, S. W., III; Joly, G. D.; Swager, T. M. *Chem. Rev.* **2007**, *107*, 1339. (c) Kim, J. M. *Macromol. Rapid Commun.* **2007**, *28*, 1191.

(5) Zuilhof, H.; Barentsen, H. M.; van Dijk, M.; Sudhölter, E. J. R.; Hoofman, R. J. O. M.; Siebbeles, L. D. A.; de Haas, M. P.; Warman, J. M. In *Supramolecular Photosensitive and Electroactive Materials*; Nalwa, H. S., Ed.; Academic Press: New York, 2001; p 339 and the references cited therein.

(6) Recent reviews: (a) Ahn, D. J.; Kim., J.-M. *Acc. Chem. Res.* **2008**, *41*, 805. (b) Sada, K.; Takeuchi, M.; Fujita, N.; Numata, M.; Shinkai, S. *Chem. Soc. Rev.* **2007**, *36*, 415.

(7) (a) Chance, R. R.; Banghman, R. H.; Muller, H.; Echhart, J. G. *J. Chem. Phys.* **1977**, *67*, 3616. (b) Galambos, A. F.; Stockton, W. B.; Koberstein, J. T.; Sen, A.; Weiss, R. A.; Russell, T. P. *Macromolecules* **1987**, *20*, 3094. (c) Tanaka, H.; Gomez, M. A.; Tonelli, A. E.; Thakur, M. *Macromolecules* **1989**, *22*, 1208. (d) Rubner, M. F.; Sandman, D. J.; Velazquez, C. *Macromolecules* **1987**, *20*, 1296. (e) Downey, M. J.; Hamill, G. P.; Rubner, M.; Sandman, D. J.; Velazques, C. S. *Makromol. Chem.* **1988**, *189*, 1199.

(8) Mino, N.; Tamura, H.; Ogawa, K. *Langmuir* **1991**, *7*, 2336.

(9) (a) Ahn, D. J.; Chae, E. H.; Lee, G. S.; Shim, H. Y.; Chang, T. E.; Ahn, K. D.; Kim, J.-M. *J. Am. Chem. Soc.* **2003**, *125*, 8976. (b) Kim, J.-M.; Lee, J. S.; Choi, H.; Sohn, D.; Ahn, D. J. *Macromolecules* **2005**, *38*, 9366. (c) Lee, S.; Kim, J.-M. *Macromolecules* **2007**, *40*, 9201. (d) Park, B. H.; Lee, J. S.; Choi, H.; Ahn, D. J.; Kim, J.-M. *Adv. Funct. Mater.* **2007**, *17*, 3447. (e) Peng, H.; Tang, J.; Pang, J.; Chen, D.; Yang, L.; Ashbaugh, H. S.; Brinker, C. J.; Yang, Z.; Lu, Y. *J. Am. Chem. Soc.* **2005**, *127*, 12782. (f) Peng, H. S.; Tang, J.; Yang, L.; Pang, J. B.; Ashbaugh, H. S.; Brinker, C. J.; Yang, Z. Z.; Lu, Y. F. *J. Am. Chem. Soc.* **2006**, *128*, 5304. (g) Lu, Y.; Yang, Y.; Sellinger, A.; Lu, M.; Huang, J.; Fan, H.; Haddad, R.; Lopez, G.; Burns, A. R.; Sasaki, D. Y.; Shelnutt, J.; Brinker, C. J. *Nature* **2001**, *410*, 913. (h) Yang, Y.; Lu, Y.; Lu, M.; Huang, J.; Haddad, R.; Xomeritakis, G.; Liu, N.; Malanoski, A. P.; Sturmayr, D.; Fan, H.; Sasaki, D. Y.; Assink, R. A.; Shelnutt, J. A.; Swol, F.; Lopez, G. P.; Burns, A. R.; Brinker, C. J. *J. Am. Chem. Soc.* **2003**, *125*, 1269. (i) Dautel, O. J.; Robitzer, M.; Lère-Porte, J.-P.; Serein-Spirau, F.; Moreau, J. J. E. *J. Am. Chem. Soc.* **2006**, *128*, 16213.

(10) (a) Matsumoto, A.; Matsumoto, A.; Kunisue, T.; Tanaka, A.; Tohnai, N.; Sada, K.; Miyata, M. *Chem. Lett.* **2004**, *33*, 96. (b) Dei, S.; Shimogaki, T.; Matsumoto, A. *Macromolecules* **2008**, *41*, 6055.

(11) (a) Matsumoto, A.; Odani, T.; Sada, K.; Miyata, M.; Tashiro, K. *Nature* **2000**, *405*, 328. (b) Odani, T.; Matsumoto, A. *Polym. J.* **2002**, *34*, 841. (c) Matsumoto, A.; Fujioka, D.; Kunisue, T. *Polym. J.* **2003**, *35*, 652. (d) Oshita, S.; Tanaka, T.; Matsumoto, A. *Chem. Lett.* **2005**, *34*, 1442. (e) Oshita, S.; Matsumoto, A. *Langmuir* **2006**, *22*, 1943.

(12) Matsumoto, A. *Polym. J.* **2003**, *35*, 93.

(13) Matsumoto, A.; Oshita, S.; Fujioka, D. *J. Am. Chem. Soc.* **2002**, *124*, 13749.

(14) Oshita, S.; Matsumoto, A. *Chem.—Eur. J.* **2006**, *12*, 2139.

(15) Dei, S.; Matsumoto, A. *Macromol. Chem. Phys.* **2009**, *210*, 11.

(16) Brandsma, L., Ed.; *Preparative Acetylenic Chemistry*, 2nd ed.; Elsevier: Amsterdam, 1988.

(17) Tadokoro, H. *Structure of Crystalline Polymers*; Wiley: New York, 1979.

(18) (a) Alberti, G.; Costantino, U.; Dionigi, C.; Murcia-Mascaros, S.; Vivani, R. *Supramol. Chem.* **1995**, *6*, 29. (b) Kanoh, K.; Shichi, T.; Takagi, K. *Chem. Lett.* **1999**, 117. (c) Takagi, K.; Saito, N.; Shichi, T.; Sawaki, Y. *Chem. Lett.* **1999**, 275. (d) O'Hare, D.; Evans, J. S. O.; Fogg, A.; O'Brien, S. *Polyhedron* **2000**, *19*, 297.

(19) (a) Matsumoto, A.; Odani, T.; Chikada, M.; Sada, K.; Miyata, M. *J. Am. Chem. Soc.* **1999**, *121*, 11122. (b) Matsumoto, A.; Nagahama, S.; Odani, T. *J. Am. Chem. Soc.* **2000**, *122*, 9109. (c) Nagahama, S.; Inoue, K.; Sada, K.; Miyata, M.; Matsumoto, A. *Cryst. Growth Des.* **2003**, *3*, 247. (d) Sada, K.; Inoue, K.; Tanaka, T.; Tanaka, A.; Epergyes, A.; Nagahama, S.; Matsumoto, A.; Miyata, M. *J. Am. Chem. Soc.* **2004**, *126*, 1764.