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Charge-Transfer Interaction between Poly(9-vinylcarbazole) and 3,5-Dinitrobenzamido Group or 3-Nitrobenzamido Group

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We studied the charge-transfer (CT) interaction between poly(9-vinylcarbazole) (PVK) and 3,5-dinitrobenzamido (DBA) group or 3-nitrobenzamido (NBA) group. The complexation equilibrium constant of PVK and *N*-butyl-3,5-dinitrobenzamide was found to be larger than that of PVK and *N*-butyl-3-nitrobenzamide using UV–vis spectroscopy. The desorption process of PVK from a DBA-modified substrate was studied with single molecule force spectroscopy. A lot of force–extension curves with a plateau were observed, which indicated the existence of trainlike conformation. The average desorption force of a PVK chain from the DBA-modified substrate was 28 pN. For comparison, the desorption process of PVK from an NBA-modified substrate was also studied, and an average desorption force of 18 pN was obtained. The apparent interaction energy of a CT complex was calculated on the basis of the desorption force and the surface density of electron acceptors. The obtained apparent interaction energies were 14 and 8 kJ·mol⁻¹ for the carbazolyl–DBA complex and carbazolyl–NBA complex, respectively. On the basis of the energy of the frontier molecular orbital of carbazole, 3,5-dinitrobenzamide, and 3-nitrobenzamide, the difference in strength between the interactions was interpreted as the influence of the substituent group on the energy of the frontier molecular orbital.

Introduction

Polymer adsorption at the liquid–solid interface is the most important step for the layer-by-layer (LbL) assembling technique, which has proved to be a versatile method for fabricating a multilayer film with controlled composition and architecture.^{1–6} The driving force for LbL assembly has been extended from electrostatic force⁷ to other secondary intermolecular interactions.^{8–11} For example, LbL assembly via hydrogen bonding was developed by Stockton and Rubner⁸ and Wang and coworkers,⁹ separately. Yamamoto et al. reported LbL assembly based on the charge-transfer (CT) interaction between the dinitrobenzoyl group and carbazolyl group.¹¹ Polymer adsorption based on electrostatic force, hydrogen bonding, and so on is already studied by many kinds of methods, while research on polymer adsorption based on CT interaction has not been reported yet.

Single molecule force spectroscopy (SMFS), which is based on atomic force microscopy (AFM), has proved to be a powerful

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technique for investigating nanomechanical properties and adsorption processes of single polymer chains.^{12–18} Different types of interactions, for example, electrostatic¹⁹ or hydrogen-bonding,²⁰ that determined adsorption processes of polymers have been characterized by SMFS. These research studies provide valuable information about the nature of noncovalent interactions and facilitate the control of polymer layer-by-layer assembly.^{19–21} Besides polymer adsorption, SMFS is effective for detecting noncovalent interaction between small molecules, such as molecular recognition,^{22,23} CT interaction,^{24,25} multiple hydrogen bonding,²⁶ and $\pi - \pi$ stacking,²⁷ through measuring rupture forces.

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Herein, inspired by Yamamoto's CT-based LbL assembly, we investigated CT interaction between poly(9-vinylcarbazole) (PVK) and 3,5-dinitrobenzamido (DBA) groups, aiming for obtaining direct information of polymer adsorption based on CT interaction. SMFS was used to study the desorption of a PVK chain from a substrate modified with DBA groups (Scheme 1). For comparison, we also studied the desorption of PVK from 3-nitrobenzamido (NBA)-modified substrate, which bore one nitro group instead of two nitro groups. The influence of substituent on CT interaction was discussed on the basis of results from several different approaches.

Experimental Section

Materials. Poly(9-vinylcarbazole) (PVK, $M_w \sim 1.1 \times 10^6 \text{ g} \cdot \text{mol}^{-1}$, PDI 3.04) and 3-nitrobenzoyl chloride (NBC, 98%) were purchased from Aldrich. 3,5-Dinitrobenzoyl chloride (DBC, 98%) was purchased from Fluka. 3-Aminopropyldimethylmethoxysilane (APS, 97%) was purchased from Acros.

N-Butyl-3,5-dinitrobenzamide (BDBA) was prepared through a condensation reaction of 1-butylamine and DBC. 1-Butylamine (7 mmol, 0.7 mL) was dissolved in 10 mL of xylene, and DBC (2 mmol, 0.53 g) dissolved in 20 mL of xylene was added dropwise. Excessive 1-butylamine was used to remove HCl generated in the condensation. The reaction mixture was stirred at room temperature for 2 h. The reaction mixture was washed with water three times and then was evaporated to remove xylene to get the raw product. The raw product was purified via silica gel column chromatography with the solvent mixture cyclohexane/ethyl acetate = 2:1 as the eluent. The product, BDBA, was a yellow solid with a yield of 60%. ¹H NMR (500 MHz, CDCl₃): δ 9.17 (1H, s, ArH), 8.95 (2H, d, ArH), 6.22 (1H, s, NH), 3.54 (2H, q, NCH₂), 1.67 (2H, m, CH₂), 1.45 (2H, m, CH₂), 0.99 (3H, t, CH₃).

N-Butyl-3-nitrobenzamide (BNBA) was prepared through a similar condensation reaction using NBC instead of DBC. The raw product was purified via silica gel column chromatography

with the solvent mixture dichloromethane/methanol = 10:1 as the eluent. The product, BNBA, was a light yellow solid with a yield of 51%. ¹H NMR (500 MHz, CDCl₃): δ 8.57 (1H, s, ArH), 8.36 (1H, d, ArH), 8.16 (1H, d, ArH), 7.65 (1H, t, ArH), 6.22 (1H, s, NH) 3.50 (2H, q, NCH₂), 1.64 (2H, m, CH₂), 1.44 (2H, m, CH₂), 0.98 (3H, t, CH₃).

Substrate Modification and SMFS Experiment. A quartz slide covered with electron acceptors (Scheme 1) was prepared as follows. A quartz slide was cleaned with a hot "piranha" solution $(H_2SO_4/30\% H_2O_2 = 7:3, (v/v))$, followed by ultrasonic cleaning thoroughly with deionized water and drying overnight in oven. (Caution! Piranha solution is highly corrosive. Extreme care should be taken when handling piranha solution, and only small quantities should be prepared.) Then the slide was silanized in the xylene solution of APS (0.1vol %) for 20 h and rinsed with benzene and dichloromethane successively. The self-assembly of APS led to an amino-covered quartz slide. 28 The slide was immersed into 0.1 M xylene solution of DBC (or NBC) for 12 h and then ultrasonic cleaned thoroughly with benzene and dichloromethane successively. After these modifications, the slide showed a characteristic UV-vis absorbance of the DBA (or 3-nitrobenzamido, NBA) group, indicating that the surface of the quartz slide was modified with plenty of electron acceptors. A time of 10 h proved enough for the modification to reach saturation. The freshly modified quartz slides were used in SMFS experiments.

A home-built SMFS instrument was set up in cooperation with Prof. Hermann E. Gaub in Ludwig-Maximilians-Universität München. SMFS experiments were carried out in a particular way as reported before.²⁹ The spring constants of Si₃N₄ tips (Veeco, Santa Barbara, CA) ranged between 20 and 35 pN·nm⁻ which were measured before each experiment using a thermal noise method.³⁰ The details of the SMFS experiment were described elsewhere.^{14,17} Briefly, PVK chains were adsorbed onto the tip from the dichloromethane solution, the concentration of which in repeat units was 1.27×10^{-5} mol·L⁻¹. A substrate modified with DBA was placed on the piezo of the SMFS instrument. Then the modified substrate was brought to contact the PVK-adsorbed tip and some polymer chains would adsorb onto the substrate. A contacting time of 1 s for the tip and the substrate proved enough to achieve the equilibrium of polymer adsorption based on CT interaction. During the separation of the tip and the substrate, PVK was desorbed from the substrate and the cantilever was deflected. At the same time, a deflection-extension curve was recorded and converted into a force-extension curve. All the force-extension curves were obtained in dichloromethane.

UV-Vis Absorption Spectroscopy and the Calculation of Interaction Energy. UV-vis absorption spectroscopy was used to determine the complexation equilibrium constant of BDBA and PVK in dichloromethane. All the UV-vis measurements were carried out on a Lambda 800 UV/vis spectrometer, Perkin-Elmer Instrument.

UV-vis absorption spectroscopy was also used to characterize the modified quartz slides and to calculate the surface density of DBA groups. UV-vis spectra of solutions of BDBA with different concentrations were measured, and the molar absorptivity of BDBA at 250 nm was calculated. Since the absorption of dichloromethane between 230 and 260 nm was strong, the mixture of dichloromethane and cyclohexane (v/v = 5:8) was used as solvent. In addition, we measured UV-vis spectra of several DBA-modified substrates. It was assumed that the molar absorptivity of DBA groups at the surface of the substrate was approximately equal to the molar absorptivity of BDBA in solution. The surface density was calculated by $d_{\rm S} = 0.5A_{250}\varepsilon_{250}^{-1}$, where $d_{\rm S}$ is

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Figure 1. UV-vis spectra for dichloromethane solutions of PVK, BDBA, and their mixtures in different concentrations. The concentrations of PVK solutions are described in repeating units.



Figure 2. Plot of $lC_{\text{BDBA}}/A_{460}^{\text{CT}}$ versus the inverse concentration of PVK. Following the method of Benesi and Hildebrand,³¹ the absorbance of the CT complex can be related to the concentration of carbazolyl groups by $lC_{\text{B}}/A_{\lambda}^{\text{CT}} = 1/\varepsilon_{\lambda} + 1/\varepsilon_{\lambda}K_{\text{eq}}^{\text{CP}}$, when $C_{\text{B}} \ll$ C_{P} . ε_{λ} is the molar absorptivity of the complex at the selected wavelength, l is the path length, and C_{B} and C_{P} are the initial concentrations of BDBA and PVK, respectively. The absorbance of the CT complex at the selected wavelength, A_{λ}^{CT} , is calculated by subtracting the absorbance of PVK and that of BDBA from the absorbance of the mixed solution of PVK and BDBA. K_{eq} is the equilibrium constant, $K_{\text{eq}} = [\text{complex}]_{\text{eq}}/[\text{BDBA}]_{\text{eq}}[\text{PVK}]_{\text{eq}}$. A linear fit of the data yields a slope of $(9.6 \pm 0.5) \times 10^{-3}$ cm·mol·L⁻¹, which gives $\varepsilon_{460} = 29 \pm 4 \text{ cm}^{-1} \cdot \text{L} \cdot \text{mol}^{-1}$ and $K_{\text{eq}} =$ $3.7 \pm 0.4 \text{ L} \cdot \text{mol}^{-1}$. The results obtained at different wavelengths are close to each other (K_{eq} calculated from the data of 450 and 470 nm are 3.5 ± 0.3 and $3.8 \pm 0.4 \text{ L} \cdot \text{mol}^{-1}$, respectively).

the surface density, A_{250} is the absorbance of the modified substrate at 250 nm, and ε_{250} is the corresponding molar absorptivity of the acceptor in solution.¹⁰ The linear density, $d_{\rm L}$, was calculated by $d_{\rm L} = d_{\rm S}^{0.5}$, using a simple square packing. Then the interaction energy was calculated by $E = N_{\rm A} F d_{\rm L}^{-1}$, where *E* is the interaction energy, $N_{\rm A}$ is the Avogadro constant, and *F* is the average desorption force.

Theoretical Calculation. The frontier molecular orbitals of model compounds were calculated at the B3LYP/6-31G(d, p) level using the Gaussian program.

Results and Discussion

BDBA was synthesized and had the same electron-acceptor group that Yamamoto et al. used in LbL assembly.¹¹ BNBA was also synthesized for investigating the influence of the substituent of the electron acceptor on the CT interaction.

CT interaction between BDBA and PVK was studied in dichloromethane, which was exactly the same solvent that Yamamoto et al. used in LbL assembly.¹¹ Figure 1 shows UV-vis absorption spectra of PVK, BDBA, and their mixtures in different concentrations. Both PVK and BDBA have weak absorption



Figure 3. UV-vis spectra for dichloromethane solutions of PVK, BNBA, and their mixtures in different concentrations. The concentrations of PVK solutions are described in repeating units.



Figure 4. Plot of $lC_{\rm BNBA}/A_{421}^{\rm CT}$ versus the inverse concentration of PVK. A linear fit of the data yields a slope of $(6.0 \pm 0.5) \times 10^{-2}$ cm·mol²·L⁻² and a *y*-axis intercept of $(8.4 \pm 0.5) \times 10^{-2}$ cm·mol·L⁻¹, which gives $\varepsilon_{421} = 12 \pm 4$ cm⁻¹·L·mol⁻¹ and $K_{\rm eq} = 1.4 \pm 0.4$ L·mol⁻¹.

in the range from 400 to 500 nm when they exist separately in solution, while the spectra of mixtures show strong absorption, and the absorbance is much stronger than the sum of the absorbance of pure PVK and BDBA at the same concentration. The increase of absorbance in the range between 400 and 500 nm indicates the formation of the CT complex. The series of spectra of BDBA mixed with different concentrations of PVK allow us to calculate the equilibrium constant, K_{eq} , of the CT complexation of BDBA and PVK, using the Benesi–Hildebrand function,³¹ as shown in Figure 2. In this way, K_{eq} for the BDBA–PVK complex is determined to be $3.7 \pm 0.4 \text{ L} \cdot \text{mol}^{-1}$.

Similarly, we studied the CT interaction between BNBA and PVK in dichloromethane, intending to study the effect of the substituent group on CT interaction. Figure 3 shows UV–vis absorption spectra of PVK, BNBA, and their mixtures in different concentrations. The increase of absorbance in the range between 400 and 500 nm in the spectra of PVK–BNBA mixtures indicates the formation of a CT complex. Using the Benesi–Hildebrand function, K_{eq} for the BNBA–PVK complex is determined to be $1.4 \pm 0.4 \text{ L} \cdot \text{mol}^{-1}$, as shown in Figure 4. It is clear that K_{eq} for the BDBA–PVK complex is larger than that for BNBA and PVK, indicating the CT interaction between BDBA and PVK is stronger. We wonder if the difference in strength between the interactions can be probed at the molecular level by SMFS.

We utilized SMFS to study the adsorption of PVK at the surface modified by DBA groups. Typical force–extension curves are shown in Figure 5. A long plateau is the common feature in these curves. Curves with a similar shape induced by other kinds of interaction instead of CT interaction were reported before.^{19,20}

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Figure 5. Representative force–extension curves of PVK desorbing from DBA-modified substrate at a stretching velocity of $500 \text{ nm} \cdot \text{s}^{-1}$. These curves are shifted vertically for convenient observation.



Figure 6. Histogram of the desorption forces of PVK from DBAmodified substrates at a stretching velocity of 500 $\text{nm} \cdot \text{s}^{-1}$. The solid line is a Gaussian fit of the histogram.

The plateau of the force curve suggests that there is a constant force for the desorption of the polymer chain from the surface, and the external energy used to separate each adsorptive point is similar. According to the plateau feature of the force curves, we can deduce that part of the PVK chain adsorbs as a trainlike conformation on the substrate.^{17b} The plateau length reflects the length of the detached part of the polymer chain from the substrate, while the height of a plateau corresponds to the desorption force that is required to detach polymers from the modified surface.^{26b} The lengths of plateaus of most curves are less than 100 nm, implying that only a small part of a polymer chain is adsorbed in a trainlike conformation. In this experiment, the force curves were obtained in dichloromethane, a good solvent of PVK. The polymer chain prefers to stay in the solvent, and a small part of the polymer chain is adsorbed onto the substrate in a trainlike conformation.

According to the statistic analysis of the plateau heights, the desorption force of PVK from the DBA-modified surface is $28 \pm 7 \text{ pN}$, as shown in Figure 6. The distribution of the plateau heights can be described by a Gaussian function, indicating the desorption of single polymer chains.¹⁷ Even when changing the stretching velocity from 500 to $2500 \text{ nm} \cdot \text{s}^{-1}$, the height of the plateau is almost the same. According to refs. 17, 26b and 32, it is inferred that the adsorption and the desorption of the polymer chains are on a much shorter time scale than the stretching process, suggesting that the experiment was performed in the equilibrium state.

Based on the chemical structures of PVK and DBA groups, we can roughly exclude the possibility of hydrogen bonding, electrostatic interaction, and coordination bonding. The carbazolyl group is relatively electron-rich and the DBA group is relatively



Figure 7. Histogram of the desorption forces of PVK from NBAmodified substrates at a stretching velocity of 500 $\text{nm} \cdot \text{s}^{-1}$. The solid line is a Gaussian fit of the histogram.

electron-poor, so that it is rational to think that the main driving force for the adsorption of PVK is CT interaction. Moreover, we used a PVK-adsorbed tip to perform a control experiment on a bare substrate without DBA groups, and the obtained force curves have no plateau.

For comparison, we studied the desorption of PVK from the substrate modified with NBA groups. Similarly, typical force–extension curves feature a long plateau, indicating that part of the PVK chain exists as a trainlike conformation on the substrate. Figure 7 shows a histogram of the desorption forces of PVK from NBA-modified substrates. The distribution of the plateau heights can also be described by a Gaussian function, indicating the desorption force determined by Gaussian function is 18 ± 6 pN. The desorption force changes significantly when PVK is adsorbed at substrate surfaces modified with different chemical groups, making it clear that the PVK chain is desorbed from the substrate rather than from the AFM tip.

In order to compare the strength of the interaction between PVK and different electron-acceptor-modified substrates, we tried to calculate the apparent interaction energy from the desorption force and the surface density of electron acceptors. According to ref 10, the surface density and linear density of electron acceptors were calculated on the basis of UV-vis spectra of both the modified substrate and the solutions. Details of the UV-vis experiment were briefly introduced in the Experimental Section. The linear density of electron acceptors on DBA-modified and NBA-modified substrates was estimated to be 1.2 and 1.4 nm⁻¹, respectively. The linear density of carbazolyl groups along the polymer chain is about 4.0 nm^{-1} , larger than that of electron acceptors; that is to say, the carbazolyl groups are excessive for CT interaction. Therefore, the interaction energy should be determined by the linear density of electron acceptors rather than that of carbazolyl groups along the polymer chain. Based on the desorption force and linear density of electron acceptors, the interaction energies were calculated to be 14 and 8 kJ·mol⁻¹ for the carbazolyl–DBA and carbazolyl–NBA complexes, respectively. The results indicate that the interaction between carbazolyl and the DBA group is stronger than that between carbazolyl and the NBA group. What we need to point out here is that we carried out the energy calculation with the only intention of comparing the two different interactions at the surface. It is not appropriate to compare this calculated interaction energy with the thermodynamic parameters. The interaction energy we calculated from the desorption force is higher than the energy based on force quantum in ref 24 by Skulason and Frisbie. Considering different molecular structures and different data analysis, the difference in energy is understandable. In our experiment, we recorded the force at the plateau and performed statistical analysis; by contrast, Skulason and Frisbie obtained a

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Figure 8. Frontier molecular orbital diagram of carbazole, dinitrobenzamide, and nitrobenzamide.

force quantum on the basis of periodicity of a pull-off force histogram.

From the results above, we can draw a conclusion that the CT interaction between BDBA and PVK is stronger than that between BNBA and PVK, and the different CT interactions can be discriminated by SMFS at the molecular level.

In order to get a better understanding to the mechanism of CT interaction, we applied frontier molecular orbital theory to provide more information on the different CT interactions. The frontier molecular orbitals of three model compounds, carbazole, dinitrobenzamide, and nitrobenzamide, were calculated.³³ The obtained highest occupied molecular orbitals (HOMOs) and lowest unoccupied molecular orbitals (LUMOs) are shown in Figure 8. The LUMO of an acceptor molecule interacts with the HOMO of a donor molecule (carbazole). The lower the LUMO level of the acceptor molecule is, the stronger the association will be.^{25,34} It is shown in Figure 8 that the LUMO level of dinitrobenzamide (0.005 eV) is lower than that of nitrobenzamide (0.035 eV), which means that the association between dinitrobenzamide and carbazole is stronger than that between nitrobenzamide and carbazole. Thus, the difference in strength between the interactions can be explained as the influence of the substituent group on the energy of the frontier molecular orbital.

Conclusion

We studied the CT interaction between poly(9-vinylcarbazole) and 3,5-dinitrobenzamido group or 3-nitrobenzamido group. The equilibrium constant of the PVK-BDBA complex was found to be larger than that of the PVK-NBA complex. The desorption force of a PVK chain from the DBA-modified substrate was determined to be 28 pN; by contrast, the desorption force of a PVK chain from the NBA-modified substrate was 18 pN. The calculated apparent interaction energy indicates that the interaction between carbazolyl and the DBA group is stronger than that between carbazolyl and the NBA group. From the energy of the frontier molecular orbitals of the three model compounds, the change in the interaction strength may be attributed to the influence of the substituent group on the energy of the frontier molecular orbital. The difference of desorption force of PVK adsorbed at different chemical modified substrates demonstrates that we can perform in situ detection of the driving force of polymer adsorption at the molecular level with SMFS, which provides valuable information for LbL assembly as well as other self-assembly processes.

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