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Evaluation of local polarity of polymer solids by a rigid fluorescent probe of carbazole–terephthalate cyclophane

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Abstract

A novel rigid fluorescent probe, carbazole–terephthalate cyclophane (Cz–TP) was applied to evaluate local dielectric constants (ε) of various polymer solids in a wide range of temperatures. For poly(vinylidene fluoride), the ε increased above the glass transition temperature (T_g), due to relaxations of the polar segment $-(CH_2CF_2)-$ of the main chain. For poly(alkyl methacrylate)s, the ε increased above the T_g or the melting temperature of the side chain, where motions of the polar ester groups are activated. For cyanoethylated polymers, the ε increased owing to motions of the polar cyano groups at the end of the side chain and the ε corresponded to the dielectric constant evaluated by dielectric relaxation measurement at a high frequency, because the Cz–TP exciplex has a lifetime of tens of nanoseconds. For a cyanoethylated polymer with a high content of cyano groups, the ε was larger at low temperatures than the dielectric constant obtained by the macroscopic dielectric relaxation measurement. These results show that the Cz–TP molecule is a useful probe for evaluation of the local polarity in polymer solids over a wide temperature range and can detect even a small change in ε at transition temperatures such as glass transition, side-chain melting, and side-chain relaxation.

Keywords: Fluorescent probe; Intramolecular exciplex; Local polarity of polymer solids

1. Introduction

Fluorescence probe techniques are widely used in various fields of photophysics, photochemistry, biology, and macromolecular science. Pyrene is one of the most famous probes, which has a characteristic sensitivity of I_1/I_3, the ratio of the first monomer emission band to the third one, to the polarity of the surrounding medium [1,2]. However this polarity probe is unsuitable for a wide temperature range, because the ratio I_1/I_3 depends on not only solvent polarity but also temperature. Electron donor (D) and acceptor (A) complexes such as a charge transfer (CT) complex and exciplex [3–5] are also used as polarity probes, because they have a large dipole moment in the excited state compared with that in the ground state. The CT fluorescence might be more sensitive to solvent polarity than exciplex emission, but the CT fluorescence is of low quantum yield and is rarely observed in polar solvents. On the contrary, exciplex fluorescence is observed in wide ranges of polarity and temperatures, indicating that it has a potential as a fluorescent polarity probe over wide polarity and temperature ranges. However, most studies on exciplex as a polarity probe have been limited to solution systems at room temperature and in particular there are few reports for polymer solids in a wide range of temperature. These limitations are due to the conformational changes in bridged D and A molecules, which cause the multiple fluorescence from various conformations or different electronic states of D and A molecules [6–9]. In general, it is difficult to evaluate the polarity of polymer solids on the basis of the fluorescent properties in solution, because conformation of D and A molecules in polymer solids should be different from that in solutions. Thus, a rigid structure is required to maintain the same conformation even in polymer solids as that in solutions.

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Cyclophanes with [2.2]linkage are suitable for solving the problem, because the structure is so rigid that there are little conformational changes in the ground and excited states over wide viscosity and temperature ranges [10,11]. Their unique structures make it easy to form π dimers with face-to-face orientations of two aromatic rings. D–A cyclophanes [12–14] having both D and A moieties are suitable model compounds for studying the photophysical properties of (CT) complexes and exciplexes based on the fixed separation and orientation of D and A moieties. Recently, we have reported fluorescent properties of a D–A cyclophane in solutions [15], which has a carbazole (Cz) donor and terephthalate (TP) acceptor in a [2.2]paracyclocarbazolophane framework. The D–A cyclophane forms an exciplex in the excited state, whose emission band sensitively depends on dielectric constants of solutions.

Here we employ the novel D–A cyclophane having Cz and TP moieties as a fluorescent probe for the evaluation of a local polarity in polymer solids. Our cyclophane has a well-defined structure with a face-to-face orientation of Cz donor and TP acceptor moieties. Furthermore, owing to the [2.2]paracyclocarbazolophane framework, there are little structural changes in the cyclophane over wide viscosity and temperature ranges [15]. Therefore, even if the cyclophane probe is doped in polymer solids, the geometrical alignment of D and A moieties, which determines fluorescent properties as a polarity probe, should be the same as that in solutions. Thus, the local polarity of polymer solids can be quantitatively evaluated over a wide temperature range on the basis of fluorescent properties of the cyclophane probe in solutions.

2. Experimental part

2.1. Materials

2.1.1. Cyclophane polarity probe

Carbazole–terephthalate cyclophane (Cz–TP) was synthesized by photodeselenation of selenacarbazolophanes. Details of the synthesis have been described elsewhere [16].

2.1.2. Solvents

Solvents used in this study were cyclohexane (Nacalai Tesque, spectroscopic grade), tetrahydrofuran (THF, Nacalai Tesque, spectroscopic grade), acetonitrile (Nacalai Tesque, spectroscopic grade).

2.1.3. Polymers

Poly(vinylidene fluoride) (PVDF, Aldrich, $M_w = 18.0 \times 10^4$, $M_n = 7.1 \times 10^4$) was purified by reprecipitation from an *N*,*N*-dimethylformamide (DMF) solution into distilled water three times. The glass transition temperature (T_g) is 233 K [17]. Poly(alkyl methacrylate)s used in this study were poly(methyl methacrylate) (PMMA, Scientific Polym. Prod., $M_w = 39.5 \times 10^4$, $T_g = 378$ K), poly(butyl methacrylate) (PBMA, Scientific Polym. Prod., $M_w = 10 \times 10^4$, $T_g = 293$ K), and poly(octadecyl methacrylate) (PODMA, $T_g = 173$ K [17], $T_m = 318$ K [18] (the melting temperature of the side chain)). All these poly(alkyl methacrylate)s were purified by reprecipitation from a benzene solution into methanol twice. Cyanoethylated hydroxypropyl cellulose (CN-HPC) obtained by cyanoethylation of hydroxypropyl cellulose was kindly provided by Professor Takeaki Miyamoto. The molar substitution (MS) of propylene oxide per anhydroglucose unit was 4.75. The nitrogen content of CN-HPC was 6.80% and $T_g = 248$ K, which were measured by elemental analysis and differential scanning calorimetry (DSC), respectively. The average number of cyanoethyl groups introduced per anhydroglucose unit was calculated to be 1.46 on the basis of nitrogen content. Cyanoethylated pullulan (CN-PUL) obtained by cyanoethylation of pullulan was a kind donation from Shin-Etsu Ltd. The nitrogen content of CN-PUL was 12.0% and $T_g = 395$ K, which were measured by the elemental analysis and DSC, respectively. The degree of substitution (DS) with cyanoethyl groups per anhydroglucose was calculated to be 2.54 on the basis of the nitrogen content.

The chemical structures of Cz–TP and polymers are shown in Fig. 1.

2.1.4. Measurements

The concentration of Cz–TP was adjusted to be in the

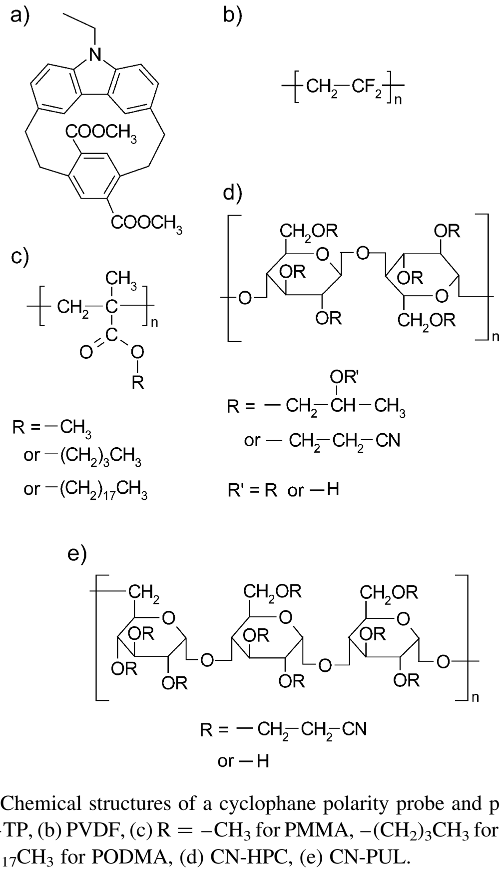

Fig. 1. Chemical structures of a cyclophane polarity probe and polymers: (a) Cz–TP, (b) PVDF, (c) R = $-CH_3$ for PMMA, $-(CH_2)_3CH_3$ for PBMA, $-(CH_2)_{17}CH_3$ for PODMA, (d) CN-HPC, (e) CN-PUL.

order of 10^{-4} mol l^{-1} in solvents and 10^{-3} mol l^{-1} in polymer solids to prevent intermolecular processes. Polymer films doped with Cz–TP were prepared on a quartz plate (15 × 15 × 1 mm) by the solution casting method for PVDF, PMMA, PBMA, CN-PUL, and CN-HPC and by the spin coating method for PODMA. Casting solvents were DMF for PVDF, benzene for PMMA and PBMA, THF for PODMA, and acetonitrile for CN-PUL and CN-HPC. Except for PVDF, polymer films prepared at room temperature were dried under vacuum for more than 12 h above the T_g. The thickness of the dried film was about 50 μm for PMMA, PBMA, CN-PUL films, 30 μm for PVDF, CN-HPC films, and 1 μm for PODMA film. For PVDF, the sample films was prepared at 60 °C with a hot plate under a nitrogen atmosphere until the DMF solvent was evaporated. The PVDF film was subsequently maintained at 95 °C for 13 h in a vacuum oven to remove the residual DMF solvent.

The temperature of the polymer film was controlled in a cryostat (Iwatani Plantech Corp., CRT510) using a PID temperature control unit (Scientific Instruments, Model 9650) from 100 to 400 K. Emission spectra were measured with a calibrated fluorescence spectrophotometer (Hitachi, F-4500). For steady-state fluorescence measurements, sample solutions and films doped with Cz–TP were excited at 310 nm.

2.1.5. Dielectric relaxation measurements of polymer matrices

The dielectric relaxation spectra were measured for CN-HPC and CN-PUL with an LCR meter (Hewlett–Packard, 4284A). Details of the measurements have been described elsewhere [19].

3. Results and discussion

3.1. Fluorescent properties of Cz–TP as polarity probe

We have previously reported fluorescent properties of the Cz–TP molecule in solutions [15]. The peak wavelength of the exciplex emission for Cz–TP is shifted to longer wavelength with increases in the dielectric constant (ε) of solvents. Fig. 2 shows emission spectra of Cz–TP in various solvents and in a PMMA film at room temperature. Similarly to the emission spectra in solvents, the emission spectrum of Cz–TP in the PMMA film was broad and structureless, indicating that the Cz–TP can form exciplex even in polymer solids where dynamic conformational changes are highly restricted compared to those in solutions. This is because the Cz–TP molecule has a rigid structure and requires little rearrangement of molecular conformation to form an exciplex. As shown in Fig. 2, the peak wavelength of the exciplex emission in the PMMA film was between that in cyclohexane (non polar solvent, $\varepsilon = 2.02$) and that in THF (moderate polar solvent, $\varepsilon = 7.58$). This finding qualitatively indicates that the local polarity of the PMMA film is low and slightly higher than that of cyclohexane. The solvent polarity dependence of the peak wavenumber can be quantitatively described by the Lippert–Mataga [20–23] formula (Eq. (1)) where $\tilde{\nu}_e$ is the wavenumber of emission maximum, $\tilde{\nu}_0$ corresponds to the emission maximum in the gas phase, ε_0 is the vacuum permittivity, h is the Planck constant, c is the velocity of the light in vacuum, ρ is the radius of a spherical solute, μ_e is the dipole moment of the solute in the excited state, ε is the dielectric constant of the solvent, and n is the refractive index of the solvent.

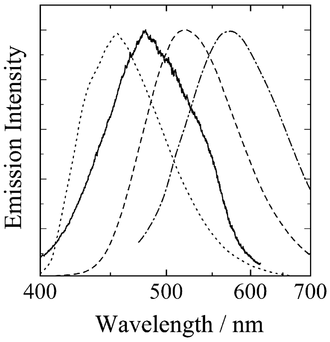

Fig. 2. Fluorescence spectra of the Cz–TP exciplex in several solvents with different polarities and PMMA polymer film: cyclohexane (dotted line); THF (broken line); acetonitrile (dashed–dotted line); PMMA (solid line), at room temperature. Emission intensity was normalized.

$$\tilde{\nu}_e = \tilde{\nu}_0 - \frac{1}{4\pi\varepsilon_0}\frac{2}{hc\rho^3}\mu_e^2 f(\varepsilon, n) \qquad (1)$$

$$f(\varepsilon, n) = \left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2}\frac{n^2 - 1}{2n^2 + 1}\right)$$

The maximum wavenumber $\tilde{\nu}_e$ of exciplex emission for Cz–TP is proportional to the polarity parameter $f(\varepsilon, n)$ of solvents over a wide range of ε [15]. Thus, on the basis of the linearity, we can evaluate ε of solvents quantitatively from the $\tilde{\nu}_e$ measured. The structure of our Cz–TP cyclophane is so rigid owing to the [2,2]paracyclocarbazolophane framework that there are little conformational changes in the ground and excited states. Therefore, even if the cyclophane probe is doped in polymer solids, the geometrical alignment of Cz donor and TP acceptor moieties, which determines fluorescent properties as a polarity probe, should be the same as that in solutions. Thus, the local polarity of polymer solids can be quantitatively evaluated over a wide temperature range on the basis of fluorescent properties in solutions.

3.2. Evaluation of local polarity of polymer solids using the Cz–TP probe

On the basis of the fluorescent properties of Cz–TP in solutions, we evaluated quantitatively the dielectric constant ε of polymer solids using the Cz–TP polarity probe. The exciplex fluorescence of Cz–TP in various polymer films was measured from 100 to 400 K.

Fig. 3 shows the temperature dependence of the Cz–TP exciplex emission in a CN-PUL polymer film from 100 to 400 K. The emission intensity monotonously decreased with increasing temperature and the peak wavelength shifted from 503 to 533 nm. From 100 to 120 K, some vibrational bands were observed and ascribed to the phosphorescence of Cz–TP. Thus, these spectra from 100 to 120 K were not used in the evaluation of ε. The value of ε for each polymer matrix was evaluated from the peak wavenumber of the exciplex emission $\tilde{\nu}_e$ by using the Lippert–Mataga relation obtained in solutions at room temperature [15], in which the refractive index of polymer matrices was assumed to be constant ($n = 1.42$ for PVDF, 1.49 for PMMA, 1.48 for PBMA, 1.46 for PODMA, 1.49 for CN-HPC, 1.50 for CN-PUL). The results are summarized in Figs. 4–6.

PVDF is a polar polymer at higher temperatures because the $-(CH_2CF_2)-$ units in the main chain have a moderate dipole moment of 1.93 D per monomer unit [24]. As shown in Fig. 4, the value of ε for PVDF increased above 230 K, which corresponds to the glass transition temperature $T_g = 233$ K of PVDF [17]. This increase in ε above T_g is due to micro-Brownian motions of polar $-(CH_2CF_2)-$ segments in the main chain caused by the main-chain relaxation in non-crystalline domains. PVDF is a semicrystalline polymer comprising the non-crystalline and crystalline regions [25]. This result indicates the Cz–TP probe is useful for selective evaluation of the local polarity in an amorphous region owing to the selective introduction not to crystal domain but to amorphous domain.

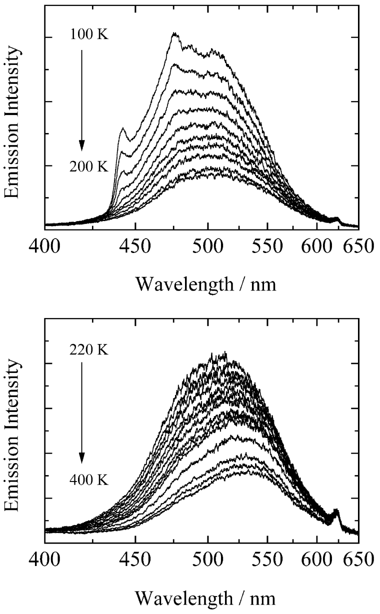

Fig. 3. Exciplex emissions of Cz–TP doped in a CN-PUL film at temperatures from 100 to 400 K. Structured emission bands at temperatures from 100 to 120 K are due to phosphorescence of the Cz–TP molecule.

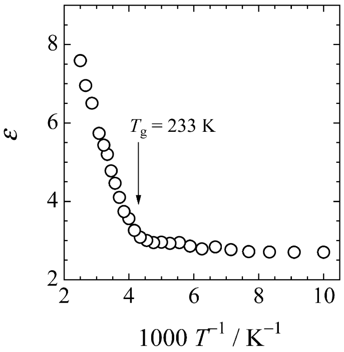

Fig. 4. Temperature dependence of ε of a PVDF film evaluated with a polarity probe of Cz–TP.

Poly(alkyl methacrylate)s have a polar group in the side chain while PVDF has in the main chain. Three kinds of poly(alkyl methacrylate)s, PMMA, PBMA, PODMA, have the same main-chain structure but different lengths of alkyl groups at the end of the side chain: $-CH_3$ for PMMA, $-(CH_2)_3CH_3$ for PBMA, and $-(CH_2)_{17}CH_3$ for PODMA. This difference results in their different glass transition temperature: $T_g = 378$ K for PMMA, 293 K for PBMA, and 173 K for PODMA. Poly(alkyl methacrylate)s are not so polar as PVDF because there is a smaller dipole moment originating from the COO ester group in the side chain (dipole moment of the COO group is estimated to be

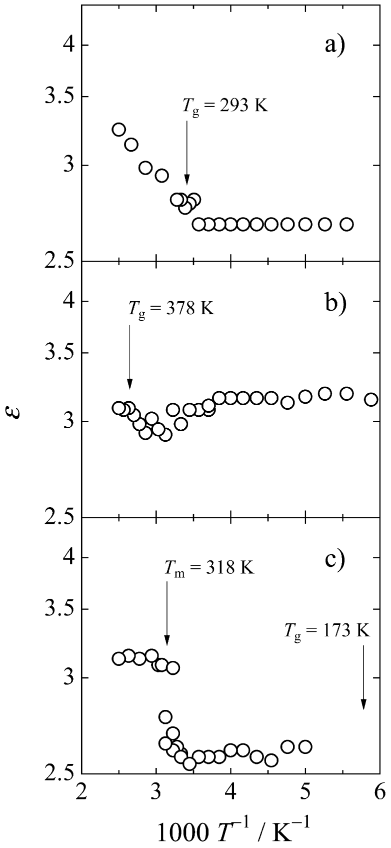

Fig. 5. Temperature dependence of ε of (a) PBMA, (b) PMMA and (c) PODMA films evaluated with a polarity probe of Cz–TP.

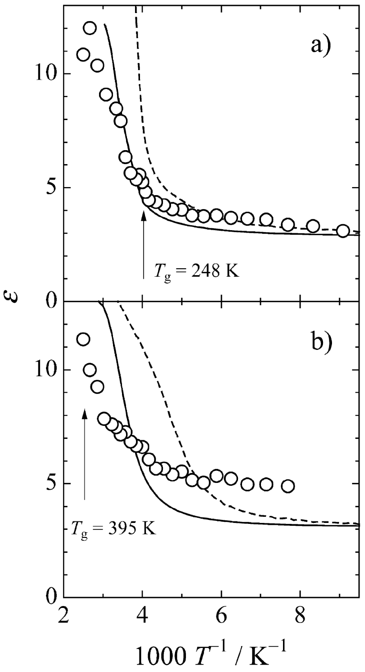

Fig. 6. Temperature dependence of ε of (a) CN-HPC and (b) CN-PUL films evaluated with a polarity probe of Cz–TP. Broken and solid lines represent the ε evaluated by the dielectric relaxation measurement at a frequency of 20 Hz and 1 MHz, respectively.

1.39 D [26]). Fig. 5(a) shows the temperature dependence of the ε of PBMA. The ε slightly increased above the T_g = 293 K although the main chain of PBMA is not polar contrary to PVDF. This increase in the ε is due to motions of the polar COO ester groups in the side chains, which are adequately enhanced by the release of main chain motions above the T_g because the ester groups are directly attached to the main chain. On the other hand, the lack of dependence of ε on temperatures below the T_g indicates that the motions of the COO ester groups are effectively suppressed by the frozen main chain. For PMMA, the value of ε was independent of temperature over the whole range of measurement (Fig. 5(b)). This is because motions of the COO ester groups in PMMA are highly restricted owing to its high T_g = 378 K. For PODMA, as shown in Fig. 5(c), the value of ε did not increase at T_g = 173 K but steeply increased around 318 K. This temperature corresponds to the melting temperature T_m of PODMA below which the long side chains of PODMA are crystallized [18]. Thus, thermal fluctuations of polar COO ester groups are drastically restricted owing to the crystallization even above the T_g. Melting of the crystallized long side chain at T_m activates both motions of side chains and main chains, resulting in thermal fluctuation of the polar COO ester groups. The steep increase in ε at T_m = 318 K reflects this phase transition of PODMA. The ε below the T_g was different in each methacrylate polymer. It decreased with increasing alkyl group length of the side chain. This decrease in the ε is probably because the density of a polar ester group in polymers is reduced with increases in the chain length of the alkyl group [26]. This trend agrees with the result from dielectric relaxation measurements, where the dielectric strength for the side-chain relaxation decreases with increasing the alkyl group length [26].

Both CN-HPC and CN-PUL are characteristic of having polar cyano groups with a large dipole moment (about 4.0 D per cyanoethyl group) [27,28] at the end of the side chains. CN-HPC shows a much lower T_g at 248 K compared with 395 K of CN-PUL, because the side chains are highly substituted with hydroxypropyl units. However, as shown in Fig. 6, the ε for both polymers increased around 200 K, irrespective of the large difference of T_g's. In both CN-HPC and CN-PUL, the increase in ε is caused by thermal fluctuations of polar cyano groups. In CN-HPC, the thermal fluctuations of polar cyano groups are activated by both main- and side-chain relaxations above the T_g, on the other hand, in CN-PUL, they are mainly activated by side-chain relaxations below the T_g [29]. The polar cyano groups having a large dipole moment are located at the end of the side chains where there is free volume and larger flexibility. This is the reason why the local motions of the polar cyano groups are activated even below the T_g.

These results demonstrate that the Cz–TP probe is sensitive to a polarity change caused by not only main-chain relaxation but also local motions of the side-chain relaxation. For the polymer having polar groups in the main chain, the local polarity increased by the thermal fluctuations induced by the main-chain motions above the T_g. For polymers having polar groups in the side chain, the local polarity increased by the thermal fluctuations induced by the main chain and/or the side chain relaxations, depending on the position of the polar group in the side chain. From these results, it is cleared that the Cz–TP molecule is useful as a polarity probe for the quantitative evaluation of a local dielectric constant of various polymer solids over a wide temperature range.

Amorphous polymer solids are inhomogeneous and have a wide distribution of relaxation time. The dielectric constant of polymer solids depends on the measuring frequency. Broken and solid curves in Fig. 6 show a dielectric constant ε obtained from dielectric relaxation measurement at frequencies of 20 Hz and 1 MHz, respectively. For CN-HPC, the values of ε evaluated using the Cz–TP probe was in good agreement with those measured at a high frequency of 1 MHz better than at a low frequency of 20 Hz. For CN-PUL, the similar tendency was observed above 250 K. These results show that the value of ε evaluated using the Cz–TP probe reflects the high-frequency motions of the polar groups. This is because the lifetime ca. 35 ns of the Cz–TP exciplex corresponds to the high-frequency motions of polar groups. A large deviation of ε for CN-PUL evaluated in high temperatures may be explained by the larger frequency distribution of the side-chain relaxation for CN-PUL than the main-chain relaxation for CN-PUL. On the other hand, as shown in Fig. 6(b), it is noteworthy that the ε evaluated below 200 K was larger than that obtained by the dielectric relaxation measurement. At low temperatures where most motions of polar groups are frozen, the dielectric constant ε should be approximately equal to the optical dielectric constant $\varepsilon_\infty = n^2 = 2.25$. However, the large ε observed below 200 K indicates the presence of local polarity originating from microscopic interaction between the polar Cz–TP exciplex and a large amount of polar cyano groups introduced in CN-PUL (DS = 2.54). The similar deviation in a local polarity from a macroscopic one has been reported for a 1,4-dioxane solution [15]. These results indicate that the Cz–TP probe method provides effective local polarities in the polymer solid, which cannot be detected by the bulk measurement such as dielectric relaxation methods.

4. Conclusions

Owing to the rigid structure of [2.2]paracyclocarbazolophane, the Cz–TP molecule is useful as a polarity probe for the evaluation of local dielectric constants of polymer solids over a wide temperature range. This probe can detect even small changes in the dielectric constant at transition temperatures in polymer solids and provides the dielectric constant due to high frequency motions of polar groups corresponding to the lifetime of the Cz–TP exciplex.

Acknowledgements

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[28] The dipole moment of a propionitrile in gas phase is reported to be 4.05 ± 0.03 D in Ref. [27], which was considered to be the same as the dipole moment of a cyanoethyl group in CN-PUL.
[29] The increase in ε around 200 K for CN-PUL was ascribed to the side-chain relaxation on the basis of dielectric relaxation measurement, which were performed at a frequency and temperature range from 0.1 to 100 kHz and 100 to 400 K, respectively. The dielectric $\tan\delta$ showed a maximum between 210 and 256 K and increased above a temperature range from 280 to 360 K. The maximum at lower temperatures is ascribable to the side-chain relaxation and the increase at higher temperatures is attributed to the main-chain relaxation.