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Glassy dynamics of hydrogen-bonded heteroditopic molecules

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ABSTRACT

A self-complementary heteroditopic molecule composed of thymine and diamidopyridine end groups and a flexible aliphatic interconnecting chain has been synthesized. The glassy dynamics of this hydrogen-bonded supramolecule have been investigated by using dielectric and rheological measurements, in combination with infra-red spectroscopy and solid-state ^{13}C NMR experiments. Decoupling of main dielectric relaxation from viscosity has been found in the vicinity of the glass transition and the temperature dependence of viscosity appears to be stronger than that of dielectric relaxation. The unusual dynamic decoupling phenomenon is ascribed to the chemical/dynamic heterogeneity and formation of hydrogen bonds in the supramolecules.

1. Introduction

Supramolecular chemistry involving nonconvalent interactions such as hydrogen-bonding and metal-ion coordination, has been increasingly used to construct diverse hierarchical structures and unique functional materials, where self-assembly relies largely on the reversible or dynamic feature of intermolecular interactions and recognition processes [1–6]. Hydrogen-bonding, as a directional and moderately strong intermolecular force, can be further employed with complementary arrangements of donors and acceptors functionality to create selectivity, allowing assembly of more elaborate structures with exceptional properties [7,8]. During the last decades, a variety of hydrogen-bonding complexes of different strengths have been designed. For example, quadruple hydrogen bonds have been used to direct polymerization of low molecular weight molecules into supramolecular polymers, where the high association constant plays a crucial role [9]. The study of hydrogen-bonding arrays is also important for understanding many biological processes, including information transfer by nucleic acids. For those hydrogen bonds with less strong associating strength, like base pairing of triple hydrogen bonds between purines and pyrimidines in DNA, more dynamic binding and unbinding processes can occur. The resulting complex dynamic nature could be potentially applicable in material science for design of smart, adaptive and self-healing materials [10–12].

One kind of triple hydrogen bonds with the strength in the medium range is based on thymine (T) and diamidopyridine (DAP) motifs. They have been attached to different polymer backbones to construct diverse structures [13,14]. Equal molar ratio mixtures of them have been found to form “polymeric”, supramolecular liquid crystalline phase [15]. However, by mixing complementary partners, the formation of complex can suffer from difficulties of careful control of stoichiometry of components. Compared to blends, single-component systems with self-complementary functionality can be better controlled without possible phase separation. This is especially important for systems with comparably low association constant when the supramolecular system becomes highly dissociated.

Many supramolecular systems appear to be glass formers [16,17], however, detailed study on the glassy dynamics of this type of system is still lacking. It is not obvious whether it can exhibit any particular behavior not observed in regular molecular or polymeric systems. In the present work, self-complementary heteroditopic (AB-type) building block (T-DAP) has been designed and successfully synthesized. A single glass transition has been observed in the whole studied temperature range. Our work focuses on the transition from liquid to glassy state. By combining broadband dielectric spectroscopy and rheological measurements, the dynamics of this hydrogen-bonded molecule in a broad time window have been investigated. Interestingly, decoupling of main dielectric relaxation from viscosity has been found in the vicinity of the glass transition. Even more surprisingly, the temperature dependence of viscosity

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appears to be stronger than that of dielectric relaxation. A mechanism underlying the unusual dynamic decoupling of this supramolecular material is discussed.

2. Experimental

2.1. Materials

The synthesis route of the heteroditopic molecule is shown in Scheme 1. Briefly, hydrogen-bonding parts composed of T and DAP are covalently connected by thiol-ene "click" chemistry. The details of synthesis and characterization are described in Supporting information. The ^{1}H NMR and ^{13}C NMR spectra of T-DAP are shown in Fig. S1a and b in supporting information, respectively.

2.2. Characterization

Thermal Analysis. Differential Scanning Calorimetry (DSC) was conducted on a TA Instruments Q1000 at a cooling rate of 5 °C/min started from 120 °C under nitrogen purge. The calorimetric glass transition temperature (T_g) was determined as the temperature of the midpoint of the heat capacity change defined by the baseline tangents.

Dielectric spectroscopy. Broadband dielectric measurements of T-DAP were performed at various temperatures started from cooling at 140 °C using a Novocontrol Concept 80 system in the frequency range of 10^{-2} to 10^7 Hz. The sample was placed between two gold-plated electrodes with a Teflon spacer of 54 μm thickness.

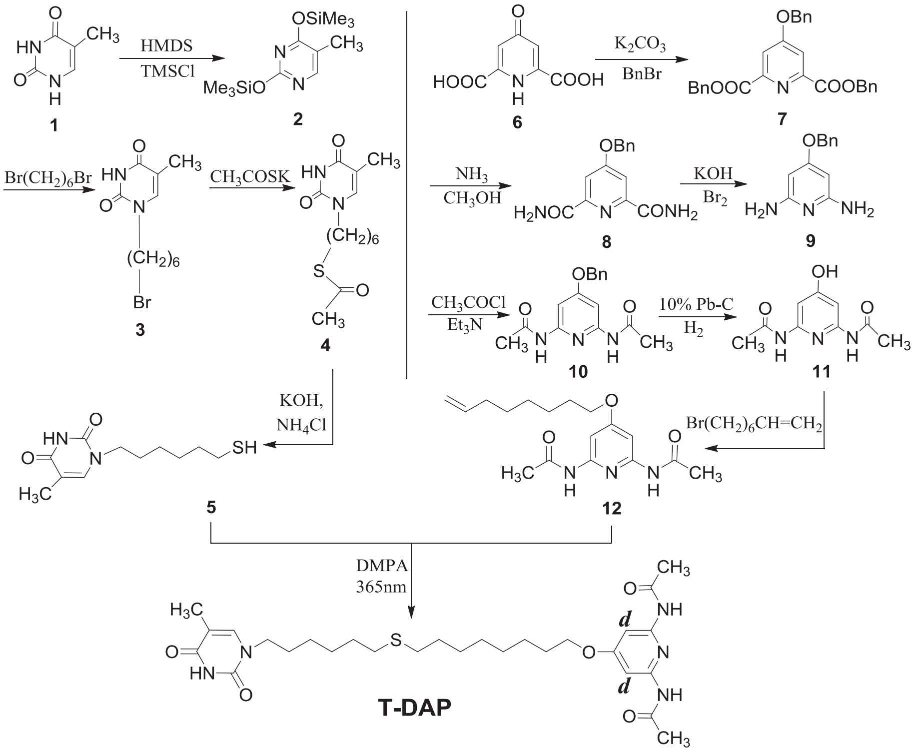
Rheological measurements. Linear creep experiments of T-DAP were performed on a TA Instruments AR2000ex rheometer with an environmental test chamber under nitrogen environment. Measurements were carried out using 8 mm parallel plates at a gap of 238–250 μm with an applied stress in the range of 0.5–20 kPa. The measurement started from cooling at 110 °C.

Infra-red spectroscopy. The infra-red (IR) spectra were acquired on a Bruker Vertex 70 V vacuum spectrometer at the resolution of 1 cm^{-1}. The sample melt was sandwiched between two KBr plates on a heating stage. The measurements started from cooling at 120 °C under vacuum (100 Pa).

Solid-State ^{13}C NMR measurements. Temperature dependent solid-state cross-polarization/magic angle spinning/dipolar decoupling (CP/MAS/DD) ^{13}C NMR measurements were carried out on a Varian Unity Inova 400 MHz spectrometer with a 4 mm T3 double resonance MAS probe. The samples were spun in nitrogen gas at 12 kHz at the magic angle. The CP contact time was 1 ms and the recycle time of the pulse was 4 s. For solids, the low sensitivity of the ^{13}C nucleus can be improved by transferring polarization from the magnetization-rich protons to ^{13}C by using cross-polarization, where the energy levels of the ^{1}H and ^{13}C spins are matched to the Hartman-Hahn condition in the rotating frame [18]. Cross-polarization is more effective to rigid structures than to mobile ones because extensive motion can reduce C–H dipolar interaction, resulting in a lower cross-polarization rate. This sensitivity of the cross-polarization experiment to more rigid components has been widely used in studies of many systems [18,19]. In the present work, selective investigation of mobility change of each component in T-DAP molecule can be accomplished. The chemical shift identifications in solid-state are referred to its solution ^{13}C NMR.

3. Results and discussion

DSC measurement has been carried out to characterize the thermal behavior of T-DAP molecules. The result of DSC measurement is presented in Fig. 1. Only a relatively broad glass transition appears between 50 and 65 °C. The midpoint of heat capacity change corresponds to a glass transition temperature of 59 °C. There is no sign of a phase transition in the entire studied



Scheme 1. Synthesis of self-complementary heteroditopic molecule T-DAP.

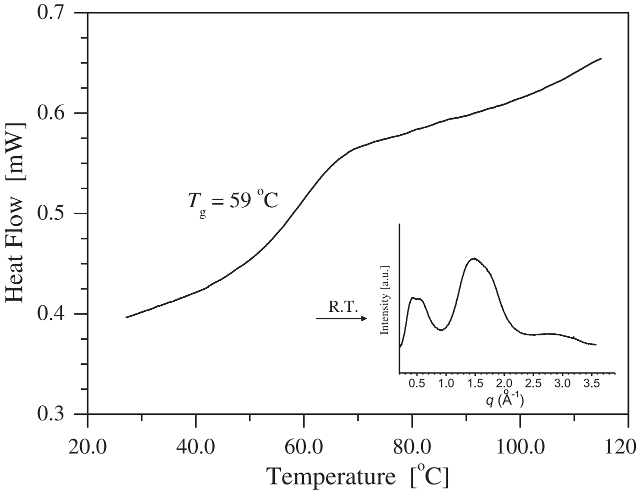


Fig. 1. DSC curve of T-DAP during cooling at 5 °C/min. Inset is the wide-angle X-ray diffraction curve of T-DAP glass at room temperature.

temperature range of 120 to −20 °C, suggesting the molecules are in an amorphous state, as also supported by the wide-angle X-ray diffraction curve shown in the inset of Fig. 1.

Since T-DAP molecule is capable to form directional triple hydrogen-bonding between T and DAP groups, the temperature dependent IR experiments can provide useful information about the changes of intermolecular hydrogen-bonding between C═O and N—H groups. Fig. 2 presents the IR spectra of T-DAP at various temperatures. N—H stretching vibration, in particular, is very sensitive to hydrogen-bonding. A very weak band around 3420 cm^{-1} ascribed to free N—H stretching can be observed at high temperatures. Its intensity decreases with decrease of temperature and eventually disappears around 80 °C. The bands around 3220 and 3260 cm^{-1} correspond to stretching vibration of hydrogen-bonded N—H of medium strength. Their intensity increases gradually with decrease of temperature. The vibration bands in the region of 1630–1700 cm^{-1} are assigned to hydrogen-bonded carbonyl groups in the thymine part. Their intensities increase with decrease of temperature. The band at 1710 cm^{-1} can be assigned to stretching vibration of non-hydrogen-bonded amide carbonyl groups in the diamidopyridine part. There is no noticeable change of this band with temperature. The positions of the asymmetric stretching of CH_2 at 2929 cm^{-1} and symmetric stretching at 2854 cm^{-1} are insensitive to temperature, either. The positions of these bands indicate that the alkyl group is disordered in the whole temperature range.

The temperature dependent IR measurements have revealed that the vast majority of the T-DAP molecules are indeed in a hydrogen-bonded state. The pronounced absorption bands at 3220 and 3260 cm^{-1} are associated with the stretching vibration of hydrogen-bonded N—H. In contrast, the free N—H peak at 3420 cm^{-1} is fairly weak at high temperatures, and disappears completely around 80 °C. On the other hand, the C═O stretching bands between 1630 and 1730 cm^{-1} indicate that most of the hydrogen bonds exist in the form of triple bonds between T and DAP groups, leaving the DAP's amide carbonyl groups free of hydrogen-bonding interactions.

When the molecules approach the glassy state, detailed description of molecular motion could help to understand the relaxation processes on microscopic level. Temperature dependent high-resolution solid-state CP/MAS/DD ^{13}C NMR is thus utilized. The results of solid-state ^{13}C NMR measurements are presented in Fig. 3. The alkyl group gives chemical shifts in the range of 20–40 ppm. No peak at ∼34 ppm indicates the amorphous order of alkyl group in the whole studied temperature range [19]. The chemical shift of aromatic rings and carbonyl groups are above 100 ppm. Specifically, carbonyl groups are in the range of 160–180 ppm, the peaks at around 95–100 ppm are assigned to the carbons *d* in DAP part, as marked in Scheme 1.

The glass transition temperature of T-DAP can be deduced from Solid-State ^{13}C NMR measurements as well. Below 60 °C, two resonant peaks of the aromatic carbon *d* can be detected at 97 and 94 ppm, while in solution it can only yield one resonance at 96 ppm, as shown in Fig. S1b. This is caused by the non-identical conformation of the carbon atoms *d* in solid-state. When temperature is higher than 60 °C, the aromatic ring can rotate freely, these two carbon atoms then become conformationally identical and only one merged resonance at 97 ppm is observed. The behavior of these two carbon atoms at high temperature thus becomes very similar to the situation in solution where no so-called packing effect exists [18]. This result is consistent with the picture that above the glass transition temperature (∼60 °C), the aromatic parts involving hydrogen-bonding can rotate freely and the alkyl part

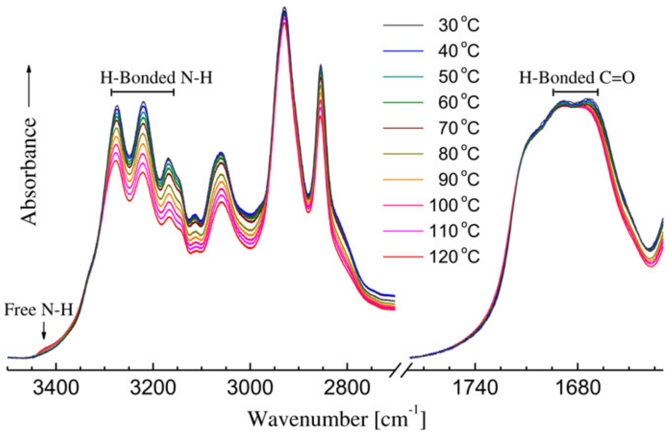


Fig. 2. IR spectra of T-DAP at various temperatures. Hydrogen-bonded N—H stretching results in characteristic bands at 3220 and 3260 cm^{-1}. The band around 3420 cm^{-1} corresponds to free N—H stretching. Bands between 1630 and 1700 cm^{-1} involve hydrogen-bonded carbonyl groups in T, while the band at 1710 cm^{-1} is from the stretching vibration of non-hydrogen-bonded amide carbonyl groups in DAP.

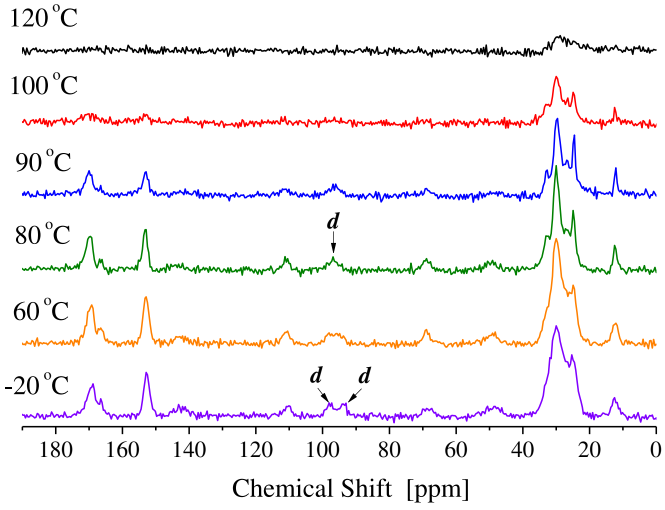


Fig. 3. Temperature dependent solid-state CP/MAS/DD ^{13}C NMR spectra of the T-DAP cooling from 120 °C.

connecting hydrogen-bonding donor and acceptor also becomes mobile.

The line-widths of all the peaks in the NMR spectra become narrower above 60 °C. This indicates that the segmental motion starts at this temperature, consistent with the glass transition temperature measured by DSC experiments. Above 100 °C the signals from the aromatic ring disappear while the aliphatic peaks still remain visible. Since cross-polarization process can distinguish different mobile components, this result implies that at 100 °C the aromatic carbon can rotate freely and become mobile. In this situation the mobile proton in the vicinity of the carbon atom can hardly enhance its signal. Therefore, no carbon atom resonance can be observed *via* cross-polarization process. Interestingly, the aliphatic signals survive at this temperature, which suggests that the aliphatic chains are still relatively rigid or not as mobile as aromatic parts at least below ∼1 nm scale. Above 120 °C, all the resonant peaks disappear, indicating that the whole molecule is mobile and flows at this temperature.

Fig. 4 shows the representative dielectric spectra of T-DAP at various temperatures. The relaxation at relatively high frequency is dominant in the whole studied temperature range, whereas the sharp rise of ε' in the low-frequency region is caused by the electrode polarization effect. The dielectric relaxation strength of this relaxation process is about 20 at 82 °C. The relaxation time τ_m is estimated from the peak frequency $f_{\max}$ of the loss spectra as: $\tau_m = 1/(2\pi f_{\max})$. The temperature dependence of the relaxation time can be fitted with the Vogel-Fulcher-Tammann (VFT) equation: $\tau_m = \tau_0 \exp[-B/(T-T_0)]$, where $\tau_0 = 2.3 \times 10^{-12}$ s, $B = 1903$ K, $T_0 = 274.5$ K.

The rheological response of the sample appears to be Newtonian in the temperature range of 60–110 °C in creep experiments, as shown in Fig. 5. No noticeable recoverable compliance has been detected. At low temperatures, a glassy compliance (J_g) shows up in our measurements. It has to be noted that the rheological tests near the glass transition are often complicated by the instrument compliance [20]. Since a systematic error due to instrument compliance at this range could exist, we choose not to discuss J_g in the present work further. However, it should be emphasized that the determination of long-time response of the material such as viscosity will not be affected.

The linear creep experiments suggest that the hydrogen-bonded assemblies are of relatively low molecular weight. The transient creep behavior of T-DAP can be well described by the Maxwell model, and the steady state compliance appears too small to be measurable in the current experimental configuration. For polystyrenes and polypropylene glycols of molecular weight higher than 4 kg/mol, appreciable recoverable compliance can be clearly detected in creep measurements [21]. The absence of recoverable compliance in this sample would suggest that the molecular weight of the hydrogen-bonded assemblies be lower than 4 kg/mol, which corresponds to only 7 repeating units. Although IR experiments suggest that the triple hydrogen bonds between T and DAP are relatively stable over the entire studied temperature range, their interaction strength may not be strong enough to form high molecular weight supramolecular polymers. The T-DAP molecules have been found to self-assemble into supramolecular complexes in deuterated chloroform with an association constant on the order of 10^2 M^{-1} [22]. The temperature dependent associate constant of T-DAP in 0.025 M deuterated chloroform solution results in ∼5 repeat units at 60 °C and ∼3 repeat units at 110 °C based on van't Hoff equation [9,22]. In the melt with the concentration of around 1.78 M, the increase of temperature from 60 °C to 110 °C will lead to decrease of degree of polymerization from 41 to 19 under the assumption that the associate constant in the melt is the same as that in deuterated chloroform and it follows the same temperature dependence. Although this assumption is crude, we can conceive that these heteroditopic molecules form supramolecular oligomers in the melt and this fairly weak hydrogen-bonding would not lead to a large population of high molecular weight supramolecular polymer. Additionally, the chain relaxation time of the supramolecular living polymer is limited by the lifetime of the individual hydrogen-bonding dynamic unit [23]. The absence of the distinguishable chain mode in the creep experiment could suggest that the lifetime of the hydrogen-bonding dynamic units be not much longer than segmental relaxation time.

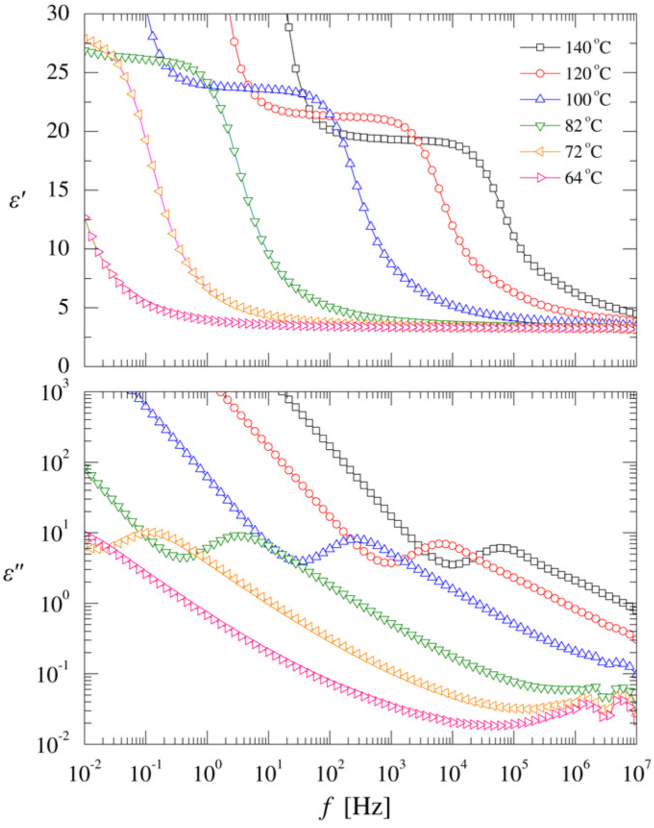


Fig. 4. Representative dielectric spectra of T-DAP at various temperatures, where the real (ε') and imaginary parts of permittivity (ε'') are plotted as a function of frequency (f).

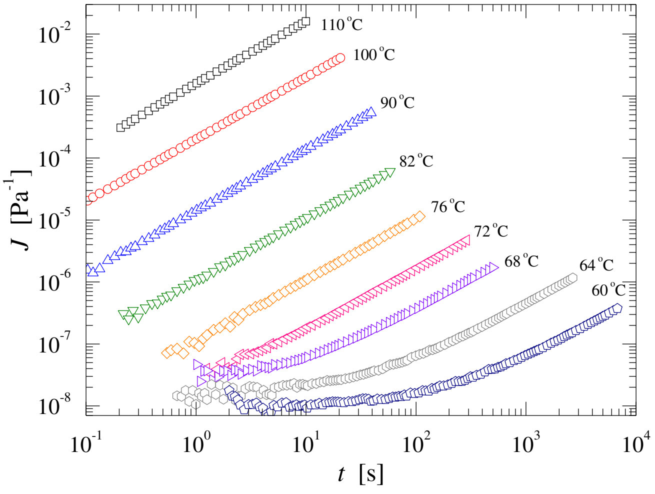


Fig. 5. Transient creep compliance (J) as a function of time (t) for T-DAP at various temperatures.

The temperature dependence of viscosity obtained from creep experiments is shown in Fig. 6. It can be well described by the VFT equation: $\eta = \eta_0\exp[B/(T-T_0)]$, where $\eta_0 = 3.32 \times 10^{-9}$ Pa s, $B = 3210$ K, and $T_0 = 258.9$ K. The glass transition temperature of T-DAP can be estimated from the VFT fitting. The viscosity of low molecular weight glass-forming liquids is typically considered to be 10^{12} Pa s at T_g [24]. The viscometric glass transition temperature is thus around 54 °C. This estimation is also in a general agreement with the DSC result, where the glass transition has been identified at 59 °C. Compared to the temperature of 62 °C obtained by extrapolation of main dielectric relaxation τ_m to 100 s, this temperature is 8 °C lower.

The most interesting finding of our current study is the different temperature dependence of viscosity and relaxation time τ_m of the main dielectric relaxation process. Fig. 6 presents shift factor a_T for η and τ_m as a function of T_g/T, where the reference temperature is 68 °C. Remarkably, the viscosity shows stronger temperature dependence than the main dielectric relaxation time. At $T_g/T = 0.80$, the a_T of η and τ_m differs roughly by a factor of 20, which indicates a substantial decoupling.

As known, when a liquid is cooled below its freezing point, its viscosity and structural relaxation time dramatically increase. Traditionally it is expected that viscosity, structural relaxation time and self-diffusion, all should have the same temperature variations in glass-forming systems. However, decoupling of self-diffusion from structural relaxation has been observed for many glass-forming liquids and decoupling of chain dynamics (including viscosity) from segmental relaxation has long been recognized in polymer melts. The segmental relaxation is typically found to have stronger temperature dependence than the chain relaxation, for polymers such as poly(polypylene glycol) [25], polyisoprene [26], and atactic polypropylene [27]. This leads to the breakdown of time–temperature superposition principle which assumes the same friction coefficient for various chain and segmental modes. The reason of the decoupling, usually happening at the dynamic crossover ~1.2 T_g, is still not clear. It has been speculated that the dynamic heterogeneity on a segmental scale might be the main reason for the different behaviors of chain and segmental dynamics [28].

Decoupling of viscosity and translational diffusion has been also found below ~1.2 T_g with generally enhanced translational self-diffusion, which leads to breakdown of the Stokes–Einstein relation (SE). Below this temperature Stokes–Einstein (SE) and Debye-Stokes-Einstein (DSE) relations grounded in classical hydrodynamics are found to be inadequate and fractional Stokes–Einstein (FSE) behavior is often observed. The FSE could be indicative of dynamic and/or chemical heterogeneity in glass and supercooled liquid on the molecular scale, where diffusion is dominated by the fastest particles whereas viscous flow is dominated by the slowest regions. For small molecular liquids, the viscosity and structural relaxation time usually have the same temperature dependence. The attempts to identify separate contribution to the viscosity arising from molecular rotational and translation motions have achieved only limited success [29].

In Fig. 7, the ratio of zero-shear viscosity η and dielectric structural relaxation time τ_α of van der Waals liquid *ortho*-terphenyl (OTP) [30,31], hydrogen-bonding glass-forming liquid glycerol [32,33], low molecular weight polymers including poly(-propylene glycol) (PPG), a weakly associated polymer whose terminal ends form hydrogen bonds, polystyrene (PS) [34,35], and η of T-DAP versus main dielectric relaxation time τ_m are demonstrated as representative examples. For typical small molecular glass-forming liquids, e.g. OTP and glycerol, their dielectric relaxation times follow the temperature dependence of viscosity. For polymers, while short PS chains show no decoupling phenomenon, the viscosity of PPG has weaker temperature dependence than dielectric relaxation, which has been discussed in terms of decoupling of segmental and chain dynamics [25]. The decoupling phenomenon observed in T-DAP clearly does not fit into either of these two categories (Fig. 7). The temperature dependence of dielectric relaxation time is found to be weaker than viscosity. The ratio of zero-shear viscosity to dielectric relaxation time increases more than one order of magnitude when the glass transition temperature is approached.

The dielectric relaxation probes the rotational dynamics of dipoles in the molecules. For T-DAP molecules, the dielectric strength is around 20 due to the large dipole moment of the hydrogen-bonding T-DAP end groups. In comparison, the contribution from the alkyl part to the dielectric spectra is relatively small. The dielectric relaxation is therefore more sensitive to local motions of the thymine and diamidopyridine. Since viscosity represents macroscopic stress relaxation, its temperature dependence could deviate from that of the local motions. The details of chemical structures could possibly lead to the different

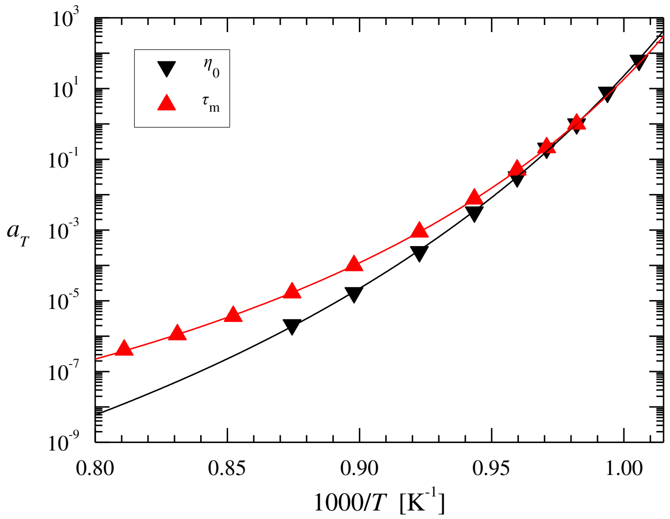


Fig. 6. Temperature dependence of shift factor a_T for η and τ_m. The reference temperature is 68 °C. Solid lines: VFT fits.

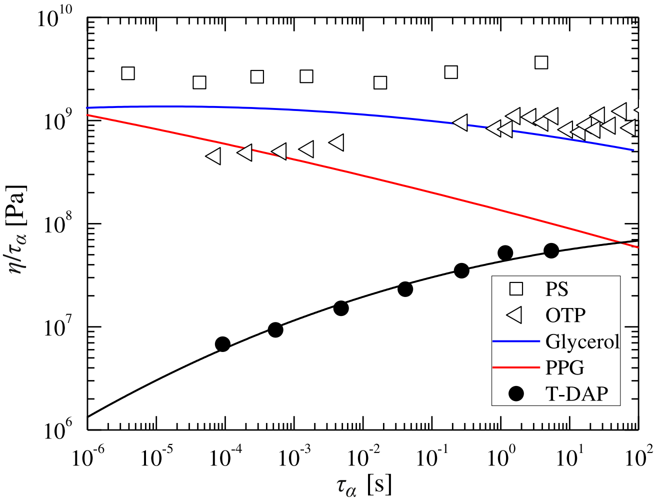


Fig. 7. The ratio of zero-shear viscosity η and α-relaxation time τ_α for polystyrene ($M_w = 3.4$ k), *o*-terphenyl (OTP), glycerol, polypropylene glycol (PPG) ($M_w = 4$ k) as a function of α-relaxation time and the ratio of zero-shear viscosity η and its main dielectric relaxation time τ_m for T-DAP.

temperature dependent behavior, as illustrated in ^{13}C NMR experiment, where the mobility of hydrogen-bonded parts is different from that of the alkyl part connecting them due to the blocky nature of this molecule.

In another aspect, this unusual decoupling may be related to the hydrogen-bonding interaction between the molecules. The probability of forming hydrogen bonds increases with decrease of temperature, which is likely to increase the probability of connection between neighbor molecules. The fraction of hydrogen-bonded molecules increases with decreasing temperature, as indicated by the characteristic bands at 3220, 3260, and 3420 cm^{-1} in IR spectra in Fig. 2. Viscous flow requires the rearrangement of the whole system, which would be affected by the formation of supramolecules through hydrogen-bonding and their collective transport, while the dielectric relaxation can proceed local motion around fluid environment. The temperature variations of the hydrogen-bonding might have a weaker effect on rotational motion of molecules than on viscosity, which reflects diffusive displacement of a center of mass. Such a phenomenon could have a general significance in supramolecular polymer systems.

According to Maxwell relationship, the ratio of the zero-shear viscosity η and structural relaxation time τ_α is often characterized as an instantaneous shear modulus (G_∞), $G_\infty = \eta/\tau$. The ratio appears to be $\sim 10^7$ Pa for T-DAP at $\tau_m = 10^{-4}$ s, which is much smaller than the typical value of organic liquids and short polymers, as shown in Fig. 7. For example, OTP, Glycerol, short chains of PS and PPG, all exhibit η/τ of the order of 1 GPa, the usual value for G_∞ of glassy materials. This unusually low value of η/τ observed for T-DAP molecules is an interesting phenomenon that might indicate that the main dielectric relaxation time could be longer than the structrual relaxation time of this supramolecular system. We hope that the investigation of this model type molecule could shed some light on the studies of complex dynamics of supramolecules and future work on the nature of this main dielectric relaxation process is underway.

4. Conclusions

Self-complimentary heteroditopic molecule has been successfully synthesized by using click-chemistry. Decoupling of the main dielectric relaxation and viscosity in the vicinity of the glass transition temperature has been observed. The viscosity shows stronger temperature dependence than that of the main dielectric relaxation, in contrast to e.g. polymers, where viscosity usually exhibits weaker temperature variations than that of the structural relaxation. This unusual behavior has been ascribed to chemical/dynamic heterogeneity and effects of hydrogen-bonding formation in this type of supramolecular material.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data related to this article can be found online at http://dx.doi.org/10.1016/j.polymer.2012.07.052.

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