

# Hydrogenation induced deviation of temperature and concentration dependences of polymer-solvent interactions in poly(vinyl chloride) and a new eco-friendly plasticizer

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Received: 22 December 2014 / Revised: 26 March 2015

Published online: 23 June 2015 – © Società Italiana di Fisica / Springer-Verlag 2015

**Abstract.** As a substitute for di-2-ethylhexyl phthalate (DOP), a new eco-friendly plasticizer, di(2-ethylhexyl) cyclohexane-1,2-dicarboxylate (DEHHP), was systematically studied in this work, mainly focusing on its interaction with poly(vinyl chloride) (PVC). The temperature and concentration dependences of polymer-solvent interactions in PVC/DEHHP were systematically investigated by rheology, low-field NMR and molecular dynamics simulations, and the results were quite different from those in PVC/DOP. With temperature increasing or PVC concentration decreasing, rheology experiments revealed that polymer-solvent interactions in PVC/DEHHP were weaker than that in PVC/DOP. Low-field <sup>1</sup>H NMR results showed that the number of polymer-solvent complexes decreased as temperature increased. A faster decreasing rate of this number made the polymer-solvent interactions weaker in PVC/DEHHP than in PVC/DOP. Molecular dynamics simulations were further performed to study the role of polymer-solvent hydrogen bonding interactions in the systems. The radial distribution function showed that heating and dilution both resulted in faster molecular motions, and disassociation of the hydrogen bonds in the simplex hydrogen bonding system. Therefore, heating and dilution had an equivalent effect on the polymer-solvent interactions.

## 1 Introduction

Poly(vinyl chloride) (PVC) products could be rigid or flexible depending on the concentration of plasticizers [1–9]. However, the rising concerns about health risk of phthalates, the most popular plasticizer, quite limited further applications of PVC. Fortunately, hydrogenation of the aromatic ring of phthalates has been proved to be an effective method to lower the potential risk [9]. In particular, hydrogen bonds had been proved to be one of the most important interactions in PVC/phthalates systems. As a simplex hydrogen bonding system [9], the poly(vinyl chloride)/di(2-ethylhexyl)

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cyclohexane-1,2-dicarboxylate (PVC/DEHHP) system is a good model for the study of the pure concentration dependence of hydrogen bonding interactions. Such interactions are influenced by many factors, *e.g.* the properties of solvents (polarity and proticity), solvent-solvent hydrogen bonds, polymer-polymer hydrogen bonds, and so on. Indeed, the concentration dependence behaviors varied in different systems [10–16]. In addition, it is also an efficient method to study hydrogen bonding interactions by molecular dynamics simulations [10–13], as it is very sensitive to the distances between two atoms. Until now, there is not a universal conclusion yet about the concentration dependence behavior of hydrogen bonds. Interestingly, in PVC/DEHHP systems, there is only one kind of hydrogen bonding interactions, *i.e.* polymer-solvent hydrogen bonds. Therefore, PVC/DEHHP could be a good model system for the study of the concentration dependence of the polymer-solvent hydrogen interactions without suffering from the influence of other kinds of hydrogen bonding interactions.

Various rheology behaviors of polymer sol/gel systems are influenced by complicated molecular interactions, which have been widely studied as a function of temperature, concentration, and type of plasticizers. Rheological behaviors around the sol-gel transition were initially studied by the groups of Winter [7,17–19] and Aoki [4,20,21]. Neutron diffraction experiments confirmed that there were three-dimensional networks in PVC gels. Guenet *et al.* [22] found the presence of sheet-like structures in the PVC/DEO (Diethyl oxalate) compounds by neutron diffraction experiments. It was also found that the fibrous crystals were expected to form networks through intermolecular aggregation [8,23–26]. Furthermore, low-field  $^1\text{H}$  NMR could also provide microscopic insights into the molecular interactions [27]. Hong *et al.* [3,28,29] used low-field  $^1\text{H}$  NMR, light scattering, and viscometer to rank the order of PVC-solvent interaction strengths in different solvents, and showed that the gelation ability of different PVC/solvent systems could indicate PVC-solvent interactions.

In our previous work, we found stronger molecular interactions in PVC/DEHHP gels than that in PVC/DOP gels, which were attributed to much more hydrogen bonding complexes and stronger hydrogen bonding interactions in PVC/DEHHP [9]. To explore the influence of hydrogenation on polymer-solvent interactions, we specifically studied the temperature and concentration dependences of hydrogen bonding interactions in PVC/DOP and PVC/DEHHP systems. The critical gelation temperatures and concentrations were obtained by rheology experiments, and thus enabled the comparison of polymer-solvent interactions. Subsequently, the low-field  $^1\text{H}$  NMR experiments were performed to get a mobility-temperature phase diagram, which clearly showed the temperature dependence of the proportion of directly interacting components. These results were further proved by molecular dynamics simulations. Herein, the combination of experiments and simulations clearly elucidated why the polymer-solvent hydrogen bonding interaction strengths decrease with dilution at a molecular level.

## 2 Experimental section

### 2.1 Materials

The PVC used in this work was laboratory-grade powders (Aldrich Chemical Co. Ltd, USA) with weight-average molecular weight  $M_w = 22.3 \times 10^4$  and number-average molecular weight  $M_n = 9.9 \times 10^4$ . The DOP and THF were chemically pure solvents (Shanghai Lingfeng Chemical Reagent Co. Ltd, China). The DEHHP was produced through the hydrogenation of DOP over supported Ni catalysts [30]. The conversion of DOP was over 99.9%.

### 2.2 Sample preparation

The two plasticized samples were prepared at room temperature with the desired amount of PVC and DOP (or DEHHP) with a large amount of THF (about 70 wt% of THF in total weight). No stabilizers were added to the solutions. They were stirred with magnetic stirrers overnight to ensure homogeneity. The evaporation of THF from each solution proceeded at room temperature for 1 week. Then each sample was dried in vacuum to get rid of residual THF until the weight became constant [1,4]. When THF was completely evaporated, transparent liquids or solid films were obtained.

### 2.3 Low-field $^1\text{H}$ NMR

The measurements were performed on a Bruker Minispec mq20 low-field spectrometer at 20 MHz proton resonance frequency. The sample temperature was controlled ( $\pm 0.1^\circ\text{C}$ ) with a BVT3000 heater working with a flow of heated air. The minispec has a typical  $\pi/2$  pulse length of about  $3\ \mu\text{s}$  and a receiver dead time of about  $13.7\ \mu\text{s}$ .

Magic-Sandwich Echo (MSE) pulse sequence was used here to get a fully refocused free-induction decay (FID) signal of the sample. This signal could be fitted with a combination of stretched and compressed exponential functions. More details of the method could be found elsewhere [9,31,32].

## 2.4 Rheology

The experiments were conducted on a HAAKE RheoStress 600 instrument. Dynamic oscillatory shear measurements were conducted by using a set of 60 mm diameter parallel plates with a sample thickness around 1.5 mm. In all the dynamic oscillatory shear measurements, the strain deformation was fixed at 0.1%, which was large enough to obtain a reasonable intensity signal, and at the same time small enough to avoid nonlinear responses. The frequency dependence of the dynamic storage modulus ( $G'$ ) and loss modulus ( $G''$ ) were measured at 20 °C and in the frequency range of 0.1–100 rad/s.

The sol-gel transition is very important to a gel system. However, it is impossible to determine the critical gelation concentration because there is no cross-over in the frequency range for all concentrations [4]. Winter's group [7,17–19] first found experimentally a scaling law of  $G'(\omega) = G''(\omega) \sim \omega^{1/2}$  at the gel point and generalized it to be

$$G'(\omega) \sim G''(\omega) \sim \omega^n \quad 0 < n < 1, \quad (1)$$

or

$$G''(\omega)/G'(\omega) = \tan \delta = \tan(n\pi/2), \quad (2)$$

for all gel systems. So, at the gel point,  $\tan \delta$  becomes independent of frequency and converges. Many experiment results have shown that this method is reliable for determining the gel point, such as the critical gelation time, temperature or concentration. Experimentally,  $n$  is found to be constant but related to the specific nature of each gel system.

## 2.5 Molecular dynamics simulations

Classical molecular dynamics simulations were carried out using the Discover molecular dynamics module of Material Studio 6.0 software package. All simulations were performed in an NPT ensemble; the Nosé-Hoover method was used to control the temperature and pressure of the simulated system. The motion equations were solved using the Verlet Leapfrog integration algorithm. Long-range electrostatic interactions were treated with the smooth particle mesh Ewald method. 2,4-dichloropentane (DCP) is a low molecular weight analog having the local conformational properties of PVC, and it has been widely studied in the literature to model PVC interactions with solvent [6]. Therefore, in this work, we utilized DCP to model PVC. The simulated system consisted of cubic boxes (side length  $L = \text{ca. } 55 \text{ \AA}$ ) with DCP and DOP mixtures. Periodic boundary conditions were applied in three directions for the simulation box. The simulations were performed using a cutoff radius of  $L/2 \text{ \AA}$  for the nonbonded interactions. Initial boxes were generated using Amorphous Cell module with a randomly inserting scheme. The energy of each box was minimized by the MINIMIZE program in the Discover module to a  $0.01 \text{ kcal mol}^{-1} \text{ \AA}^{-1}$  rms gradient. Subsequently, a run of 100 ps (a time step of 1 fs) in the NPT ensemble at 298 K and 1 atm was carried out. The first 20 ps running was used to achieve equilibration, which was checked through constant energy, and the remaining 80 ps running was for data collection.

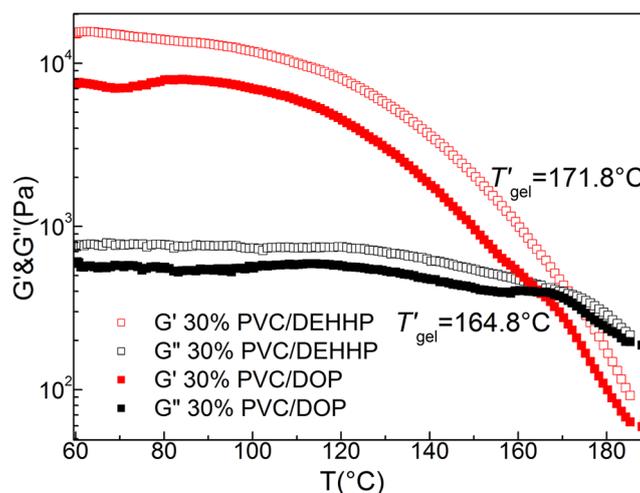
## 3 Results and discussion

### 3.1 The temperature dependences of interactions of two PVC gels

#### 3.1.1 Rheology experiments

PVC can form thermally reversible physical gels with numerous solvents, and the gels will turn into solutions with increasing the temperature. This sol-gel transition is remarkably reflected in the rheological behavior, where there are significant changes in both shear storage modulus  $G'$  and loss modulus  $G''$ . In our previous work [9], these two systems exhibited different fractions of intermediate components at a PVC concentration of 30 wt%. Thus, in order to obtain comparative results, the moduli of two PVC gels as a function of temperature are shown in fig. 1 with a PVC concentration of 30 wt%.

At low temperatures, both systems exhibited larger  $G'$  and smaller  $G''$ , indicating a typical gel behavior. With temperature increasing,  $G'$  and  $G''$  both decreased slowly. When the temperature was high enough,  $G'$  decreased rapidly and formed a cross-over with  $G''$ ; thus the systems transformed from solid-like gels to liquid-like solutions. In general, it is necessary to plot the frequency dependence curve of the loss tangent ( $\tan \delta$ ) under different temperatures in order to accurately determine the critical gelation temperature,  $T_{\text{gel}}$ , as  $\tan \delta$  converged at  $T_{\text{gel}}$  [4]. However, the gelation ability differs much in the two systems. Therefore, the crossover of  $G'$  and  $G''$  curves could be roughly utilized to determine the critical gelation temperature,  $T'_{\text{gel}}$ , and thus to compare their gelation ability. It is apparent that  $T'_{\text{gel}}$  of PVC/DEHHP is much higher (ca. 7 °C) than that of the PVC/DOP system.



**Fig. 1.** Curves of storage moduli  $G'$  (red) and loss moduli  $G''$  (black) of PVC/DEHHP (hollow squares) and PVC/DOP (solid squares) as a function of temperature with a PVC concentration of 30 wt%. The frequency of the measurement is 1 Hz. The heating rate is  $2^\circ\text{C}/\text{min}$ .

The gelation ability is closely related with the polymer-solvent interactions. According to Guenet's works [8, 22–26], the PVC gel was indicated as a three-dimensional cross-linked network with relatively free solvents inside. The network was composed of small crystallite domains and flexible PVC chains, which resulted from intermolecular aggregations. According to the widely accepted percolation theory [33], the gel fraction,  $G$ , which is the ratio of the molecular contents in a gel macromolecule to the total molecular contents, can be expressed by

$$G \propto (p_c - p)^\beta \quad \text{for } p < p_c \quad (3)$$

and

$$G \propto (p - p_c)^\beta \quad \text{for } p > p_c, \quad (4)$$

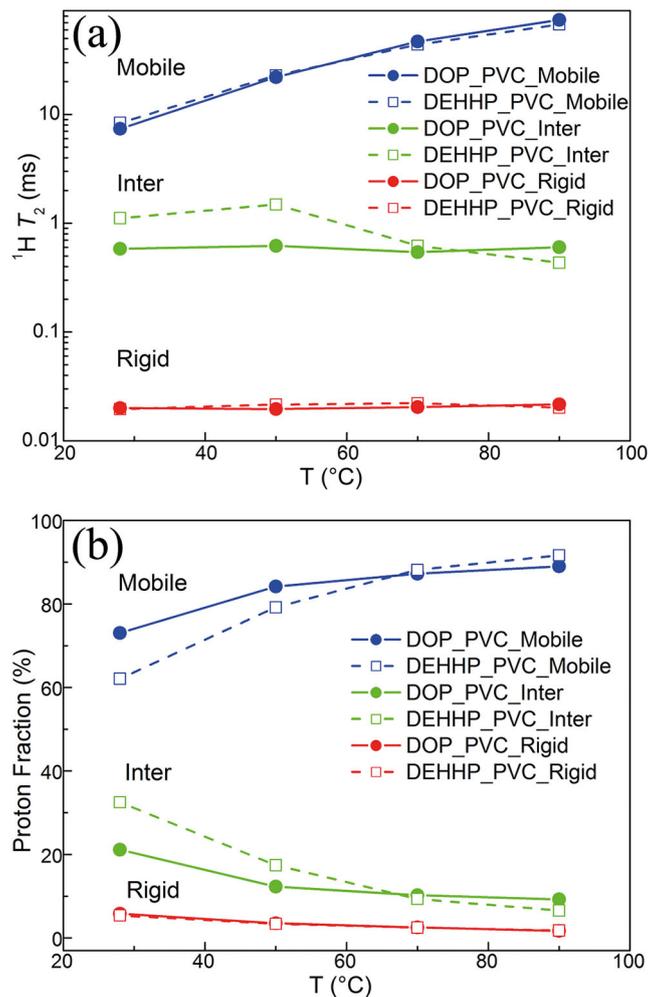
where  $p$  is the conversion factor, *i.e.*, the probability of the formation of bonds between nearest neighbors of monomers.  $p_c$  is the critical conversion factor required for gelation, and  $\beta$  is a critical exponent ( $\beta = 0.45$  for a three-dimensional lattice model). Once  $p$  is increased to reach  $p_c$ , many small clusters will turn into a percolating cluster, *i.e.* a cluster spanning the whole sample, and thus the sol-gel transition takes place [34]. To a certain polymer, weak polymer-solvent interactions could lead to the polymer chain aggregation rather than dispersion in solvents, indicating a higher  $p$  [3]. When polymer-solvent interaction is enough weak, a integrated network will form when  $p$  reaches the critical value  $p_c$ , and the sol-gel transition occurs.

On the basis of previous work [3, 28, 29] and the percolation theory [33], for PVC gels with different solvents, higher gelation ability generally associates with weaker polymer-solvent interactions. In the above two gel systems, PVC/DEHHP had a higher  $T'_{\text{gel}}$  than PVC/DOP, which meant that PVC/DEHHP system had stronger gelation ability. Therefore, at high temperatures around  $T'_{\text{gel}}$ , the polymer-solvent interactions in PVC/DEHHP should be weaker than that in PVC/DOP. This result was just unexpectedly opposite to what we obtained in the previous work which indicated stronger interactions in PVC/DEHHP [9]. Herein, it could be concluded that the polymer-solvent interactions in two gel systems changed a lot with increasing the temperature.

The main interactions between PVC and two plasticizers were confirmed to be hydrogen bonds in the form of Cl-C-H...O=C complex in our previous work [9]. Generally, increasing the temperature will lead to faster molecular motions. Consequently, the intermolecular hydrogen bonds would be disassociated to a certain extent, and the polymer-solvent interactions became weak. Therefore, it could be inferred that the influence of increased temperatures on intermolecular hydrogen bonds in PVC/DEHHP was much larger than that in PVC/DOP, rendering the interactions in PVC/DEHHP weaker than that in PVC/DOP at higher temperatures.

### 3.1.2 Low-field $^1\text{H}$ NMR experiments

To gain insight into the details of this change of polymer-solvent interactions with increasing the temperature, and to confirm the above inference, low-field  $^1\text{H}$  NMR was employed to study the two heterogeneous gel systems. Spin-spin relaxation time ( $T_2$ ) is sensitive to the molecular mobilities of the sample [35, 36], as it is mainly determined by the  $^1\text{H}$ - $^1\text{H}$  dipolar couplings. Herein, in this study we utilized MSE sequence to fully refocus the FID signal of rigid



**Fig. 2.** The temperature dependence of each component's (a) apparent  $T_2$  and (b) proton fraction for PVC/DOP and PVC/DEHHP gels at a PVC concentration of 30 wt%. The solid points represent PVC/DOP and the hollow ones represent PVC/DEHHP.

components, and Hahn Echo sequence to record the signal of mobile components by eliminating the effects of field inhomogeneity as well as chemical shift anisotropy. It was found that in both plasticized systems the proton FID signals came from three distinct components at a temperature well above the glass transition temperature ( $T_g \ll 0^\circ\text{C}$ ).

In order to get more detailed insights into each component, the FID signal could be fitted with a Gaussian function, a Weibull function and an exponential function, assuming that there are three different components.

$$A(t) = A_0 [f_{\text{rigid}} \exp(-t/T_{2,\text{rigid}})^2 + f_{\text{inter}} \exp(-t/T_{2,\text{inter}})^a + f_{\text{mobile}} \exp(-t/T_{2,\text{mobile}})], \quad (5)$$

where  $f_{\text{rigid}}$ ,  $f_{\text{inter}}$  and  $f_{\text{mobile}}$  were the fractions of the rigid, intermediate and mobile components with corresponding apparent spin-spin relaxation time  $T_{2,\text{rigid}}$ ,  $T_{2,\text{inter}}$  and  $T_{2,\text{mobile}}$ . The  $T_2$  relaxation time and the fraction of each component at different given temperatures were shown in fig. 2.

When the PVC concentration was low, the contents of rigid and intermediate components were also very low, and they were insensitive to temperatures. According to the results of previous work [9], we chose the gels at a PVC concentration of 30 wt% because of the largest difference in the fraction of intermediate components between the two gel systems at this PVC concentration.

According to our previous work [9], the rigid components of gels consisted of the microcrystal and/or rigid amorphous polymer chains below the glass transition temperature. In fact, it corresponded to the cross-linking domains of the three-dimensional network. The rigid components of both gels showed the same  $T_2 \sim 0.02$  ms, which meant that the rigid component did not go through obvious changes in the experimental temperature range. Moreover, the fraction of rigid components was the same for both PVC/DEHHP and PVC/DOP systems, which slightly decreased with increasing temperature. Therefore, it could be concluded that the rigid cross-linking domains did not have direct

interactions with the solvents, and the slight molecular structure difference between two plasticizers did not influence the rigid cross-linking domains.

The mobile components of the two systems also had the coincident  $T_2$  in the range from ca. 7 ms to ca. 70 ms with the temperature increasing. According to our previous work [1], this long  $T_2$  indicated that the mobile components mainly consisted of free solvent molecules. The nearly equal  $T_2$  relaxation times at different temperatures indicated that these two similar plasticizers also had the same mobility. But the difference in the proton fraction of mobile components showed that PVC/DOP system had much more free solvents at low temperatures. Moreover, the PVC/DEHHP system turned out to have more free solvents at high temperatures, as shown in fig. 2(b).

The intermediate component consisted of flexible PVC chains and restricted solvents. The PVC chains and solvents interacted with each other and combined together to form a component with the mobility between rigid and mobile ones. Therefore, its fraction can be directly related to the number of interacted complexes. At low temperatures, the fraction of intermediate component ( $f_{\text{inter}}$ ) of PVC/DEHHP was much larger than that of PVC/DOP. As temperature increased,  $f_{\text{inter}}$  of both gels decreased but distinctly. Furthermore,  $f_{\text{inter}}$  of PVC/DEHHP decreased more rapidly than that of PVC/DOP, and became smaller than that of PVC/DOP at higher temperatures. There was a crossover point at around 70 °C. These two different behaviors of  $f_{\text{inter}}$  with increasing temperatures clearly confirmed our previous inference in sect. 3.1.1, that the increased temperatures had a larger influence on intermolecular hydrogen bonds in PVC/DEHHP than in the PVC/DOP system. It clearly indicated that the number of polymer-solvent complexes in PVC/DEHHP reduced much faster than that of the PVC/DOP system with increasing the temperature.

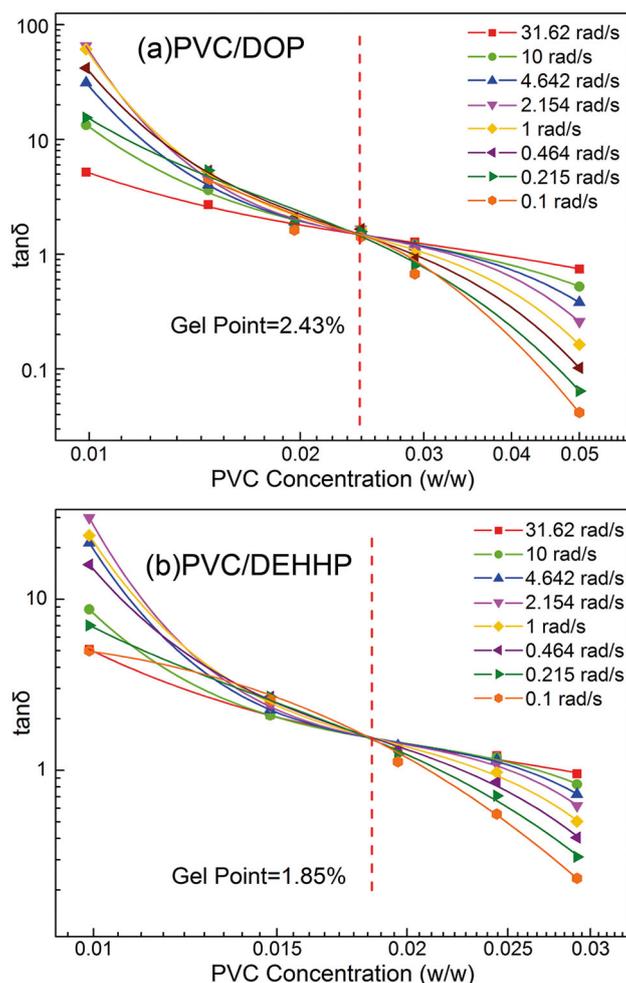
Furthermore, the  $T_2$  relaxation time of the intermediate components ( $T_{2,\text{inter}}$ ) for the two gels exhibited similar behaviors as a function of temperature.  $T_2$ , in principle, is determined by the residual  $^1\text{H}$ - $^1\text{H}$  dipolar couplings, which could well indicate the molecular mobility of the corresponding components. With the temperature increasing, molecular mobility would increase, leading to a long  $T_2$ . However, besides the temperature, the number of hydrogen bonding complexes would also affect the molecular mobility. Therefore, as the temperature increased, the number of restricted solvents per polymer chain decreased, which resulted in a lower mobility and shorter  $T_{2,\text{inter}}$ . In other words, increasing the temperature will certainly enhance the mobility of the whole system.  $T_{2,\text{mobile}}$  and  $f_{\text{mobile}}$  both increased while the rigid component still remained the same. Therefore, if the increased mobility was mainly contributed by the mobile components,  $T_{2,\text{inter}}$  would remain the same or even decrease. For the PVC/DOP gel in the experimental temperature range, the effects of the temperature and the number of hydrogen bonding complexes are almost counteracted, and  $T_{2,\text{inter}}$  is nearly unchanged. For the PVC/DEHHP gel, similar to  $f_{\text{inter}}$ ,  $T_{2,\text{inter}}$  was initially longer than that of PVC/DOP, and then became shorter at high temperatures. The crossover point was also around 70 °C. It suggests that the number of complexes decreasing factor becomes of major influence. Therefore, in comparison with PVC/DOP, the number of polymer-solvent complexes in PVC/DEHHP decreased faster with increasing the temperature. This result was consistent with the temperature dependence behavior of  $f_{\text{inter}}$ . They together confirm the assumption in the previous rheology experiment (sect. 3.1.1).

## 3.2 The concentration dependences of hydrogen bonding interactions in two PVC gels

### 3.2.1 Rheology experiments

Generally for a thermally reversible polymer gel, the sol-gel transition is dependent on temperature, concentration, and molecular weight. The net effects of these three parameters on the sol-gel transition are actually the same. Therefore, dilution is another way to transform a polymer from the gel phase to the solution phase. In order to find out whether there are still dependence behaviors of the polymer-solvent interactions in the two gel systems when concentration decreases, the critical gelation concentration was determined by rheology experiments. Since the crossover point of  $G'(\omega)$  and  $G''(\omega)$  was dependent on frequency, the definition of the gel point by this traditional method is not accurate enough here. The method described in eqs. (1) and (2) has to be adopted in this work.

The plots of loss tangent  $\tan \delta$  versus PVC concentration for different frequencies were shown in fig. 3. All curves under different frequencies converged to one point under certain polymer concentrations. At this point,  $\tan \delta$  lost its dependence on frequency and became a constant, and thus this point was defined as the gel point. The critical gelation concentrations for both gel systems were accurately determined by this method. As shown in fig. 3, the critical gelation concentration of PVC/DEHHP ( $\sim 1.85$  wt%) is lower than that of PVC/DOP ( $\sim 2.43$  wt%). The difference is not huge but obvious enough via this accurate method. At low PVC concentrations, this higher gelation ability of PVC/DEHHP indicated weaker polymer-solvent interactions. Interestingly, it was also just in opposition to the results in our previous work, which proved stronger interactions in PVC/DEHHP. The interesting results of different concentration dependence behaviors of polymer-solvent interactions were in good agreement with the results of their critical gelation temperatures. This relationship between the gel point and polymer-solvent interactions is not only concluded from percolation theory but it has also been confirmed by experiments. Hong [3,28,29] measured gel points of different PVC/solvent systems. The molecular interactions were also studied by static light scattering analysis and low-field  $^1\text{H}$  NMR. The degree of the molecular interaction is PVC/THF > PVC/MOR > PVC/DOA in order, where it was found that higher gelation ability corresponded to weaker polymer-solvent interactions.



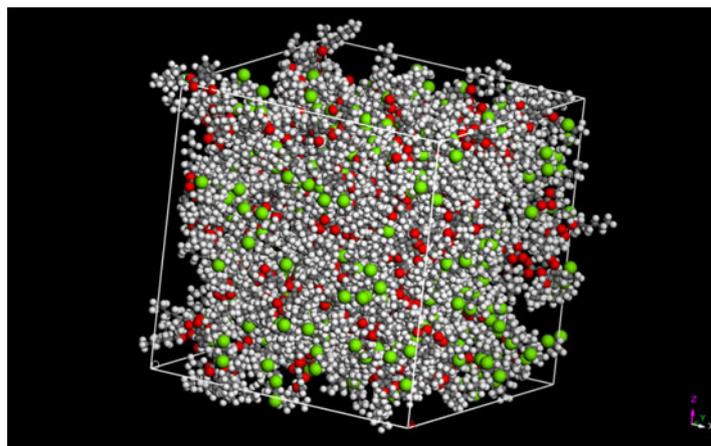
**Fig. 3.** Loss tangent  $\tan \delta$  of (a) PVC/DOP and (b) PVC/DEHHP as a function of PVC concentration for various angular frequency  $\omega$  as indicated.

In the phase diagram of a polymer-solvent binary mixture, the polymer concentration and system temperature are two parameters which co-determine whether the mixture to be in a solution phase or gel phase. Therefore, changing polymer concentration or temperatures should have the equal effect on the sol-gel transition [33]. It can be expected that decreasing concentration had similar influence on the polymer-solvent interactions as increasing the temperatures. However, it is difficult to study the concentration dependence of the polymer-solvent interactions. Especially for PVC solution, only a few studies were reported. Hassun’s group [37] used ultrasonic velocity technology to study PVC/THF solutions, and the Srinivasarao group [5] used the same technology to study PVC/DMF solutions in 0–3 wt% PVC concentration. Both groups found that polymer-solvent interactions decreased as PVC concentration was decreased, which was consistent with our above inference. However, to PVC systems with solvents of large molecular sizes, there are no conclusive results to confirm that the polymer-solvent interactions decreased with dilution or any reliable theory to elucidate this phenomenon.

### 3.2.2 Discussion of low-field $^1\text{H}$ NMR results

In comparison with the low-field  $^1\text{H}$  NMR experimental results in our previous work [9], in view of the apparent difference in proton fraction of intermediate components, it has been proved that the polymer-solvent interactions were stronger in PVC/DEHHP than those in PVC/DOP in a wide concentration range. However, the proton fraction of intermediate components ( $f_{\text{inter}}$ ) corresponded to the number of PVC-solvent complexes, and could not be precisely narrowed down to a single PVC chain. Therefore  $f_{\text{inter}}$  could not provide useful information at low concentrations.

Herein, in this study we preferred to focus on the concentration dependence of  $T_{2,\text{inter}}$ , which corresponded to the averaged mobility of a single PVC chain and restricted solvents. The rigid components corresponding to the cross-linking domains just kept the original behaviors in the solid state. The mobile component corresponded to the



**Fig. 4.** The snapshot of the simulated PVC/DOP system at a 30 wt% PVC concentration after minimization. Red, green, yellow and blue spheres represent O, Cl, C, and H atoms, respectively.

free solvents trapped in the network formed by intermolecular aggregations of PVC chains. Decreasing the PVC concentration would weaken this trapping effect and lead to a higher mobility of the mobile components. Therefore,  $T_{2,\text{mobile}}$  increased when PVC concentration decreased, and the curve of  $T_{2,\text{mobile}}$  against concentrations follow a straight line on a log-linear scale.

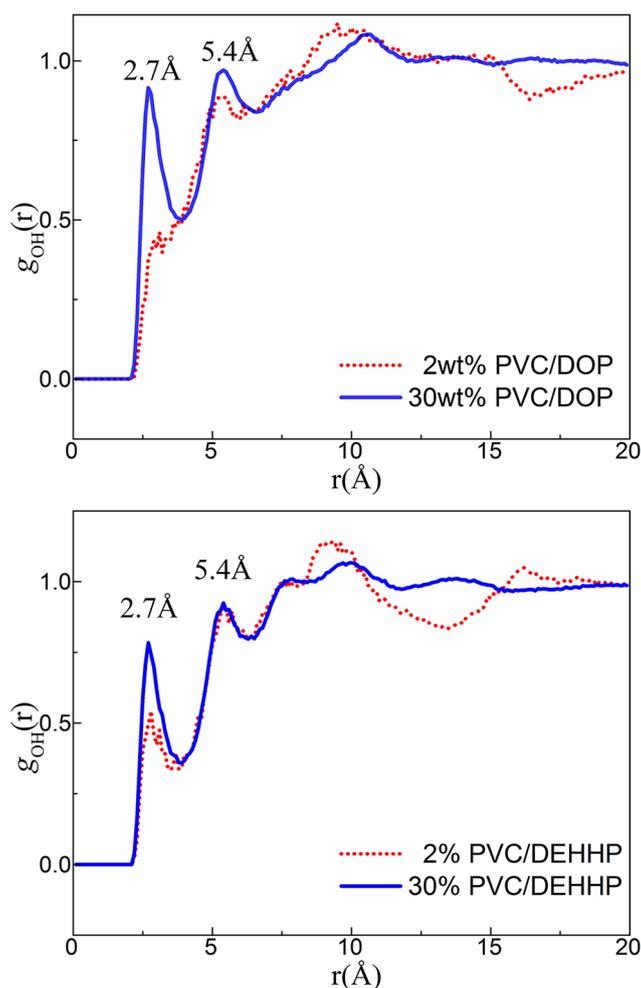
For the intermediate components, the decreased intermolecular aggregation would also increase the mobility. As was discussed in sect. 3.1.2, there was another factor that influenced the  $T_{2,\text{inter}}$  relaxation time, *i.e.* the number of restricted plasticizers per PVC chain. In the concentration range from 15 wt% to 70 wt%,  $T_{2,\text{inter}}$  showed the same behavior as  $T_{2,\text{mobile}}$ , linearly increasing with the concentration. It indicated that the change of the number of restricted plasticizer molecules per PVC chain played a minor role in comparison with the concentration factor. When PVC concentration is below 15 wt%,  $T_{2,\text{inter}}$  diverged evidently from previous straight line and had a decreasing trend. This significant change indicated that the number of restricted solvents per PVC chain reduced a lot at low concentrations, which greatly affected  $T_{2,\text{inter}}$ . Therefore, the concentration dependences of  $T_{2,\text{inter}}$  for both systems proved that the polymer-solvent interactions got weaker as PVC concentration decreased, which was in good agreement with our rheology results, and strongly supported our inference that decreasing concentration had similar influence on the polymer-solvent interactions as increasing the temperature.

### 3.2.3 Molecular dynamics (MD) simulations

The difference in critical gelation concentration only indicated the different concentration dependence behaviors of the polymer-solvent interactions, and low-field  $^1\text{H}$  NMR results only provide an indirect proof at a molecular level. Therefore, both methods can't give direct details about the change of polymer-solvent interactions between a concentrated gel and a dilute solution. To confirm whether the polymer-solvent interactions became weaker as concentration decreasing, MD simulations were further performed. Since concentration variation should be based on a system with certain volume, MD simulations were more productive than quantum chemistry calculations. It could provide abundant information about hydrogen bonding interactions at a molecular level. Herein, we used MD simulations to study two PVC/DOP systems at different PVC concentrations. In order to keep consistency with previous experiments, we chose a 30 wt% PVC concentration for the concentrated gel and 2 wt% PVC concentration for the dilute solution. 2,4-dichloropentane (DCP) was adopted to model PVC. The snapshot of the system structure after minimization is shown in fig. 4.

After the initial 20 ps running, the coordinates of all atoms were recorded every time step. On the basis of our previous work, the main polymer-solvent interactions here are hydrogen bonds in the form of Cl-C-H...O=C complex. Furthermore, there are not any other forms of polymer-solvent interactions. Therefore, the O...H radial distribution function (RDF) of DCP and DOP(DEHHP) was calculated as shown in fig. 5, which provided the probability of finding a carbonyl oxygen atom of DOP(DEHHP) at a distance  $r$  from the  $\alpha$ -H atom of DCP.

As shown in fig. 5, for the 30 wt% PVC/solvent system, there were several obvious peaks, of which the maximum was located at 2.7 Å. The first strong peak is undoubtedly due to the hydrogen bond interactions between PVC and solvents. The most probable distance 2.7 Å, *i.e.* the probable hydrogen bond length, was also in good agreement with the hydrogen bond length 2.74 Å obtained from NBO analysis by Gaussian software in our previous work [9]. Apart from the first shell contributed by the first peak, the second peak with a maximum at 5.4 Å and the third peak around 10.4–10.7 Å indicated outer shells with weaker interactions, which can be related to the network structures



**Fig. 5.** O...H Radial distribution function of DCP/DOP (top) and DCP/DEHHP (bottom) at different PVC concentrations.

of the gel. On the contrary, for the 2 wt% PVC/DOP simulated systems, there are only very minor first peaks in the range 0–4 Å. It meant that there were no stable hydrogen bonding interactions between the selected O and H atoms. Correspondingly, the second peak intensity decreases, and the third peak broadens, compared to the 30 wt% PVC/DOP system. It is probably related to the disassociation of network structures of the gels. PVC/DEHHP also exhibited similar behavior. The differences of the radial distribution for the two systems proved that the number of hydrogen bonds decreased markedly with PVC concentration decreasing. This result is consistent with our conclusion in the previous section that polymer-solvent interactions became weaker with decreasing the polymer concentration. It is also consistent with results obtained from other PVC/solvent systems reported by the groups of Hassun [37] and Srinivasarao [5]. Therefore, it is the first direct proof about the concentration dependence of simplex hydrogen bonding interactions without other interferences.

The rheology, low-field  $^1\text{H}$  NMR and the MD simulation results together confirmed the equivalent effect of temperature and concentration on polymer-solvent interactions. On the basis of existing results, more details could be inferred about the influence of dilutions on the hydrogen-bonding interactions. The low-field  $^1\text{H}$  NMR results proved that the mobility of both intermediate and mobile components increased as PVC concentration decreased. Specifically, the gel system consisted of PVC network formed by intermolecular aggregation of PVC chains. Dilution would introduce more free solvents to weaken this aggregation and reduce the degree of cross-linking. Therefore, both the flexible polymer chains and the restricted solvents (intermediate component) had increased mobility, *i.e.* faster molecular motions. The local free solvents (mobile components) with increased mobility would also further enhance the molecular motions of the complexes. The direct RDF proof from MD simulations showed that the existing hydrogen bonds in mixture were almost disassociated when the PVC concentration decreased from 30 wt% to 2 wt%. According to the latest IUPAC definition of hydrogen bonds, “The Gibbs energy of formation for the hydrogen bond should be greater than the thermal energy of the system for the hydrogen bond to be detected experimentally” [38]. This definition is usually related to the temperature effect. Without doubt that increased temperature will result in the disassociation

of hydrogen bonds. On contrast, the complex hydrogen bonding interactions and strong bonding energy often make the concentration effect negligible in most situations. However, since the hydrogen bonds between PVC and solvents are not strong here, below a certain concentration, the thermal energy of local molecules can be larger than the binding energy of hydrogen bonds and make the hydrogen bonds disassociated. In another word, the hydrogen bonds become thermally unstable at low PVC concentration, just the same as at high temperature.

## Conclusions

In this work, the hydrogenation influence on the intermolecular interactions between PVC and two plasticizers, DOP and DEHHP, was first studied systematically focusing on the temperature and concentration effects. The rheological experimental results showed that PVC/DEHHP had stronger gelation ability, which indicated weaker polymer-solvent interactions at high temperatures or low concentrations for PVC/DEHHP. The low-field  $^1\text{H}$  NMR results confirmed the interesting different temperature dependence behaviors of polymer-solvent interactions in the PVC/DEHHP and PVC/DOP systems. It also proved that heating caused the reduction of the number of polymer-solvent complexes in both gel systems. The temperature effect on PVC/DEHHP system was much stronger than that on PVC/DOP. On the other hand, for concentration effect, the results of low-field  $^1\text{H}$  NMR experiments and molecular dynamics simulations together showed that dilution enhanced the molecular motions, which resulted in the disassociation of the hydrogen bonds at very low concentrations. It firstly confirmed that the polymer-solvent hydrogen bonding interactions got weaker without other interferences when the PVC concentration was decreased in PVC/DOP system. This result could also be applied to other PVC/phthalate systems or similar polymer/solvent systems with simplex hydrogen bonds. In conclusion, for both PVC/DEHHP and PVC/DOP gel systems, increasing temperature and decreasing PVC concentration have equivalent effect on the polymer-solvent interactions. In particular, the polymer-solvent interactions in PVC/DEHHP became weaker than that in PVC/DEHHP when the temperature was high or the concentration was low.

## Author contribution statement

All authors contributed equally to the paper.

## Notes

The authors declare no competing financial interest.

We would like to thank Ziqi Tian (Nanjing University) for discussions of molecular dynamics simulations. We also appreciate the financial support of National Basic Research Program of China (973 program, 2012CB821503) and Program for Changjiang Scholars and Innovative Research Team in University. This work was also supported by the National Natural Science Foundation of China (51133002, 21174062, 21274060, 21273105 and 21074052), the foundation research project of Jiangsu province (BK20131269) and MSTC (2013AA031703) of China.

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