



# The strong interaction between poly(vinyl chloride) and a new eco-friendly plasticizer: A combined experiment and calculation study



Yang Liu<sup>a</sup>, Rongchun Zhang<sup>b</sup>, Xiaoliang Wang<sup>a,\*</sup>, Pingchuan Sun<sup>c</sup>, Wei Chen<sup>a</sup>, Jianyi Shen<sup>d</sup>, Gi Xue<sup>a,\*</sup>

<sup>a</sup> Key Laboratory of High Performance Polymer Materials and Technology, Nanjing National Laboratory of Microstructures, Department of Polymer Science and Engineering, The School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

<sup>b</sup> School of Physics, Nankai University, Tianjin 300071, PR China

<sup>c</sup> Key Laboratory of Functional Polymer Materials, Ministry of Education, College of Chemistry, Nankai University, Tianjin 300071, PR China

<sup>d</sup> Laboratory of Mesoscopic Chemistry, The School of Chemistry and Chemical Engineering, Nanjing University, Nanjing 210093, PR China

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## ABSTRACT

Hydrogenation has been proved to be an efficient way to remove the toxicity of phthalate plasticizer. However, other influences of this hydrogenation are still unknown. Here we chose di-2-ethylhexyl phthalate (DOP) and di(2-ethylhexyl) cyclohexane-1,2-dicarboxylate (DEHHP) to study the influence on interaction with poly(vinyl chloride) (PVC). By combining experiment and calculation, we found the interaction was stronger in PVC/DEHHP than in PVC/DOP. Low-Field <sup>1</sup>H NMR results showed that PVC chains could restrict much more DEHHP molecules than DOP. FTIR results showed that the interaction exists in form of hydrogen bonding complex, and it was stronger in PVC/DEHHP than in PVC/DOP system. Combined with FTIR results, theoretical calculation results revealed the three-center hydrogen bonded structure of the complex. Both the proportion and the binding energy of pre-complex in DEHHP are much larger than in DOP. Here, the hydrogenation-induced change of interaction was elucidated systematically and could be generalized to other phthalate plasticizers.

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## 1. Introduction

Poly(vinyl chloride) (PVC) is the one of the most widely produced plastic. Phthalates especially di-2-ethylhexyl phthalate (DOP) are main plasticizers. The raising concerns about health risks of phthalates limited the use of plasticized PVC in many areas such as medical devices, toys and food packages. To solve this problem, some scientists hydrogenated the benzene ring of phthalates in order to break the parahormone structure [1,2]. Some new eco-friendly plasticizers have been obtained in this way. So the next problem is what changes results from the hydrogenation and whether this kind of hydrogenated phthalates could functionally replace the old ones. Crespo [3] studied the optimal curing conditions and mechanical performance of di(isononyl) cyclohexane-1,2-dicarboxylate (DINCH) and DOP. But there is still a lack of theoretical support and microscopic evidence. Therefore we focused on the change of interaction resulting from the hydrogenation and

carried out a comparative study of di(2-ethylhexyl) cyclohexane-1,2-dicarboxylate (DEHHP) [4] and DOP.

PVC/plasticizer system has been studied for many years. Generally PVC/plasticizer system is classified as a three-dimensional cross-linked network of flexible PVC chains. And the PVC crystals work as the cross-linking domains [5,6]. Rheology is very helpful to learn the network properties. Winter [7–10] first found a precise method to determine the gel point and used it to study PVC gels. By the same method, Aoki [6,11,12] observed PVC/DOP gel rheological behavior before, near, beyond the sol–gel transition as a function of concentration, temperature and molecular weight. He obtained the scaling exponent  $n = 0.75$  which is independent of temperature and molecular weight. The interaction between the PVC and the plasticizer plays a very important role in many behaviors of the system. Low-Field <sup>1</sup>H NMR is a widely used method to characterize interaction. Hong [5] discovered three components which are separated from CPMG decaying signals for PVC/Chlorobenzene gels. W. Barendswaard [13] found two kinds of PVC chains with different mobility in PVC/DOP (50/50 wt%) system by combing Solid Echo and Hahn Echo pulse sequence together. Guenet [14] found the evidence of sheet-like structure for the compound of PVC/DEO by neutron diffraction. Koenig [15] used

\* Corresponding authors. Tel.: +86 025 83686136.

E-mail addresses: [wangxiaoliang@nju.edu.cn](mailto:wangxiaoliang@nju.edu.cn) (X. Wang), [xuegi@nju.edu.cn](mailto:xuegi@nju.edu.cn) (G. Xue).

FTIR technique and found complexes formation of the type C=O...Cl—C between the carbonyl of the DOP and the chloride atom of PVC. In Garnaik's work [16],  $^1\text{H}$  NMR was employed to find the chemical shift evidence for hydrogen bond between PVC and DOP. To obtain direct insight into molecular scale, Coughlin [17] obtained the PVC–plasticizer intermolecular energies and the theoretical diffusion coefficients of different phthalates by theoretical calculation.

In our previous work [18,19], we found DOP has a special effect to PVC chain due to its large molecular size, which is different from small molecule solvent such as THF. DOP can prevent PVC chain entanglement and furthermore increase its crystallinity.

The intermolecular interaction has always been the research focus [20–24]. However, only a partial picture of the interaction between PVC and plasticizer was shown till now. To get an overall view of interaction between PVC and DEHHP/DOP at both macro and molecular scale, we combined experiment and calculation. In this work Low-Field  $^1\text{H}$  NMR was employed to give a phase diagram of mobility, which would show proportion of the direct interacted component. Regarding the sensitive displacement of carbonyl stretching frequency, FTIR was used to confirm the type of interaction and compare their interaction strength qualitatively. Based on these experiments, theoretical calculation at molecular scale was used to simulate this situation of interacted complex. The theoretical calculation directly gave the interacted complex structure, quantitative interaction energy and other original evidences to support two previous experimental results. Both experiment and theoretical calculation together elucidated how this hydrogenation influences the interaction.

## 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 (Shanghai Lingfeng Chemical Reagent Co., Ltd., China). The DEHHP was produced through the hydrogenation of DOP over supported Ni catalysts [4]. The conversion of DOP was over 99.9%.

### 2.2. Experiment

The two plasticized samples were prepared at room temperature with desired amount of PVC and DOP (or DEHHP) with 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 over a night to ensure the homogeneity. The evaporation of THF from each solution proceeded at room temperature for 1 week. Then each sample was dried in vacuum until the weight became constant to get rid of residual THF [6,19]. After THF evaporated completely, 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 ( $\pm 0.1$  °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  $\mu\text{s}$ .

As the receiver of the minispec has a rather long dead time of 13.7  $\mu\text{s}$ , the initial part of the free induction decay (FID) reflecting the rapidly decaying rigid-phase signals is missing, as shown in

Fig. 1a. This problem is tackled by the Magic-Sandwich Echo (MSE) pulse sequence shown in Fig. 1b and the FID can be well refocused [25]. MSE–FID is very sensitive to the inhomogeneity of magnetic field and not accurate when relaxation time is long. Interestingly, a Hahn Echo sequence which has the dead time problem can well eliminate this inhomogeneity. We cut off the longer part (80–10<sup>6</sup>  $\mu\text{s}$ ) of MSE–FID and the shorter part (0–80  $\mu\text{s}$ ) of Hahn Echo. Then the rest FID were normalized and connected to each other. During this process, we made sure the new FID curve smooth around the connection point. Fully refocused FID could be obtained in this way. And spin–spin relaxation time,  $T_2$ , was determined by this method. Fully refocused FID could be well fitted with a combination of stretched and compressed exponential functions [26,27].

$$M(t) = \sum M_i \exp[-(t/\tau)^a] \quad (1)$$

Therefore, an exponent with  $a = 2$  (Gaussian) along with a very short (20–40  $\mu\text{s}$ )  $\tau$  indicates a rigid component, while  $a \sim 1$  or even less (indicating a  $\tau$  distribution) and longer  $\tau$  indicate a mobile component. Intermediate component is just between them with an exponent between 2 and 1 (Weibull). Since all proton signals were detected, the NMR intensity is proportional to the number of total protons [28–30].

### 2.4. Fourier transform infrared spectroscopy

The infrared spectra were obtained on a Bruker Tensor 27 Fourier transform Infrared Spectrometer. At room temperature, each spectrum was recorded at a resolution of 2  $\text{cm}^{-1}$  with a total of 100 scans. The samples for examining were prepared from THF solution evaporated on KBr plates by similar method in the previous experiment section.

### 2.5. Theoretical calculation

The calculations were performed by using Gaussian09 software package [31]. Based on former researchers' studies [13,15] and our FTIR results, the main interaction between plasticizer and PVC chain in the complex originates from hydrogen bond or electrostatic interaction. Hydrogen bonded complexes are also dominated by electrostatic interactions, and thus traditional density functionals are capable of computing acceptable binding energies. M06-2X method provides significant improvements over traditional density functional for hydrogen bond because of its ability to capture "medium-range" ( $\leq 5$  Å) electron correlation [32,33]. So M06-2X method with 6-31++g(d,p) basis set was chosen to optimize the local minimums and calculate this interaction. Gibbs free energy at 298 K and 1 atm could be obtained by frequency calculation. Natural charge could be computed to reveal the charge distribution of the molecule. It is based on the construction of a set of "natural atomic orbitals" (NAOs) for a given molecule in an arbitrary atomic orbital basis set [34,35]. Vibrational frequency was scaled by a factor equal to 0.947 to reproduce the FTIR spectrum.

## 3. Results and discussion

### 3.1. Low field $^1\text{H}$ NMR experiment

The PVC/plasticizer system has a three-dimensional network with different domains. Such different domains accompany the different mobility originating from interaction between solvent and polymer. Spin–spin relaxation time ( $T_2$ ) is sensitive to characterize the different mobilities of the sample [36,37], especially in the low field. Traditionally, due to the dead time restriction, Hahn Echo pulse

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