



# Neutral dipole-dipole dimers: A new field in science



Edward M. Kosower\*, Galina Borz

School of Chemistry, Tel Aviv University, Tel Aviv, Israel

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## ABSTRACT

Dimer formation with dipole neutralization produces species such as low polarity water (LPW) compatible with hydrophobic surfaces (Phys. Chem. Chem. Phys. 2015, 17, 24895–24900) Dimerization and dipole neutralization occurs for *N*-methylacetamide on polyethylene, a behavior drastically different from its conformation in acetonitrile on AgBr:AgCl planar crystals (AgX) (ChemPhysChem 2014, 15, 3598–3607).

The weak infrared absorption of the amide dimer on polyethylene is shown experimentally. Dimerization of palmitic acid is shown along with some of the many ramifications for intracellular systems. Polyoligomers of water are present on polyethylene surfaces. Some high resolution spectra of three of the polyoligomers of water are shown along with a mechanistic scheme for polyoligomer formation and dissolution. The structures of some of the oligomers are known from spectroscopic studies of water on AgX.

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## 1. Introduction

After thin film IR studies on polar silver bromide silver chloride (AgX) crystalline surfaces [1] to examine a material with a non-polar hydrophobic surface, polyethylene film (PE). To our surprise, we found strong peaks of water, many of which we could recognize as water oligomers from our previous research using AgX [1]. To explain the presence of these oligomers on a hydrophobic surface, we proposed and found evidence for an intermediary low polarity form of water (LPW), a dipole-dipole dimer in which the dipoles neutralize one another [2]. The implications of the presence of neutral dimers are profound and we herein report some of them, including an unprecedented dimerization of *N*-methylamides (*N*-methylacetamide, NMA) as well as the known dimerization of carboxylic acids (palmitic acid, PA). *N*-methylacetamide (NMA), a material with a high permittivity (“dielectric constant”, 178.5 (30 °C) [3] forms a  $3_{10}$ -helix in acetonitrile on a silver halide surface. The  $3_{10}$ -helix soon converts to an  $\alpha$ -helix and then to a  $\pi$ -helix, a process readily followed by IR. Eventually a planar arrangement is produced [4]. In contrast, addition of NMA to a PE film leads to a weakly absorbing material in which the peaks of many water polyoligomers are still visible and even increase in number for additional NMA. The weak absorbances show that dipole dimers have been formed and that **they do not mix with the water oligomers or polyoligomers!!!** NMA dimers can be constructed so as to minimize the net dipole moment (calculated to be between 0.31 D and 0.98 D), in contrast to the hydrogen-bonded dimer (8.96 D), the latter known

from gas-phase studies [5]. The apposed dimer is illustrated in Fig. 1A and the H-bonded dimer is shown in Fig. 1B. The low-polarity dimer model has mildly polar methyl groups enclosing an area with a low dipole moment, and is thus compatible with the hydrophobic surface of PE.

### 1.1. Scope of the Article

A	Polyethylene (PE) Should be <b>Hydrophobic</b>	Infrared spectra (IR)	→ Carries H <sub>2</sub> O as <b>Oligomers (O) and Polyoligomers (PO)</b>	→ Mediated by <b>Dipole Dimer Low Polarity Water (LPW)</b>
B	<b>Surface Behavior</b> Scheme relating Oligomers and Polyoligomers	<b>Dimers</b> <i>N</i> -methylacetamide (NMA) (NMAD)(NTAD) Carries H <sub>2</sub> O (O + PO + LPW)		<b>Dimers</b> Palmitic Acid (PA)(PAD) Carries H <sub>2</sub> O (O + PO + LPW)
C	Water Oligomers	<b>NMA/CH<sub>3</sub>CN</b>		<b>Polyoligomer Numbers</b> <b>Signal Variation</b> <b>Space Variation</b>
	Hexamers <b>Boat/Chair/Books1,2</b>	$3_{10} > \alpha > \pi$ -Helices		

NMA: CH<sub>3</sub>CONHCH<sub>3</sub>; NTA: (CH<sub>3</sub>)<sub>3</sub>CCONHCH<sub>3</sub>; PA: CH<sub>3</sub>(CH<sub>2</sub>)<sub>14</sub>COOH

The scope of the article begins with PE, generally accepted as hydrophobic. The IR of PE revealed not only that water was present but that it appeared in two forms, oligomers (O) and polyoligomers (PO). How did we recognize what they were? These species had been observed as

\* Corresponding author.

E-mail address: [kosower@post.tau.ac.il](mailto:kosower@post.tau.ac.il) (E.M. Kosower).

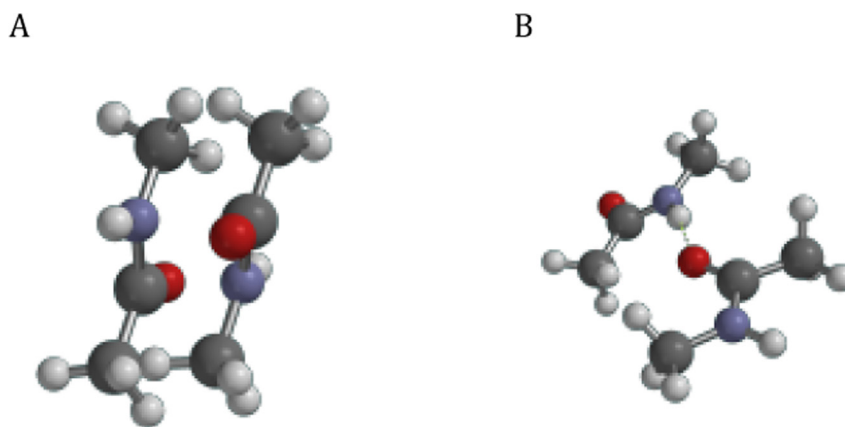


Fig. 1. (A) The low-polarity dimer of NMA. (B) The H-bonded dimer of NMA.

especially strong “marker” peaks in the spectra<sup>1</sup> of water placed on planar AgX, a platform developed by Katzir and his coworkers [6]. But there was a problem: the proximity to PE of oligomers with substantial (calculated) dipole moments and thus polarity, including cyclic hexamers of water (chair and boat forms), the cyclic pentamer, the books I and II, and the cyclic trimer [7a]. Another link was needed, a role perfectly fit by the already cited low polarity water (LPW). The choice was experimentally supported by the detection of low intensity absorption in the bending region.

Some important generalities flow from these results. What other dimers might be present in the biological or chemical world? Palmitic acid dimer (PAD) would be a candidate for decreasing the polarity of the acid (PA). Another possibility might be *N*-methylacetyl amides of which we have noted *N*-methylacetamide (NMA). We had found that NMA in a polar solvent on AgX was very acrobatic, forming first a  $3_{10}$ -helix, an  $\alpha$ -helix, a  $\pi$ -helix and a planar form in succession. In sharp contrast, we discovered that NMA forms a dimer (NMAD) and becomes immiscible with the water present on the PE surface. One may vary the acyl group and even include functional groups. Another aspect of the surface behavior of water is the formation of oligomers and polyoligomers. We will show a diagram that explains the formation of polyoligomers from oligomers and their ultimate formation of oligomers with apposed dipoles. This Scope summary should make it easier to follow the description of the varied phenomena found for the PE-water system.

## 2. Results and Discussion

We first show the spectra of polyethylene in the bending region of water ( $1500\text{--}1800\text{ cm}^{-1}$ ) in Fig. 2. The strong peaks are located at positions corresponding to “marker peaks” in many cases (for example,  $1540\text{ cm}^{-1}$  [1], cyclic hexamer (chair form) and  $1560\text{ cm}^{-1}$ , cyclic hexamer (boat form)) while the lower peaks are due to oligomers, some identified. The number of high peaks varies somewhat, and the two spectra (Fig. 2A, 11 peaks and Fig. 2B, 12 peaks) are typical for PE. Expansion of the wavelength scales reveals the detailed spectra of some of the oligomers. The results provide strong support for the identities in the case of the chair and boat forms of the hexamers.

A structure for the chair form of the water hexamer together with the experimental absorption peaks is shown in Fig. 3. The calculated and experimental absorption peaks are given in the caption to the figure.

The expansions of the PE IR spectra are shown in Fig. 4A and B for the books I and II ( $1504\text{--}1510\text{ cm}^{-1}$ ), the chair cyclic hexamer ( $1537\text{--}1543\text{ cm}^{-1}$ ) and the boat cyclic hexamer ( $1556\text{--}1562\text{ cm}^{-1}$ ). The resolution used is  $0.5\text{ cm}^{-1}$ . The assignments for the chair form of the water hexamer are given in Fig. 3. The peak pattern for the chair water hexamers is precisely what one should expect, with three peaks for the chair (which cannot be parallel to the PE plane, since the top and bottom water molecules are (a) not identical and (b) shifted about 2 and  $4\text{ cm}^{-1}$  respectively from the central peaks). There are two sets of

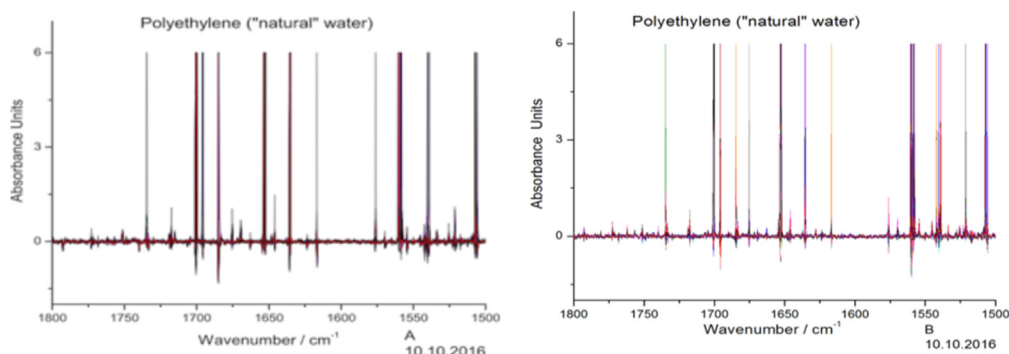


Fig. 2. Two sets of infrared spectra of “natural water” on polyethylene in the water bending region. The “lines” represent polyoligomer absorption peaks over 50 scans of 0.1 s each.

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