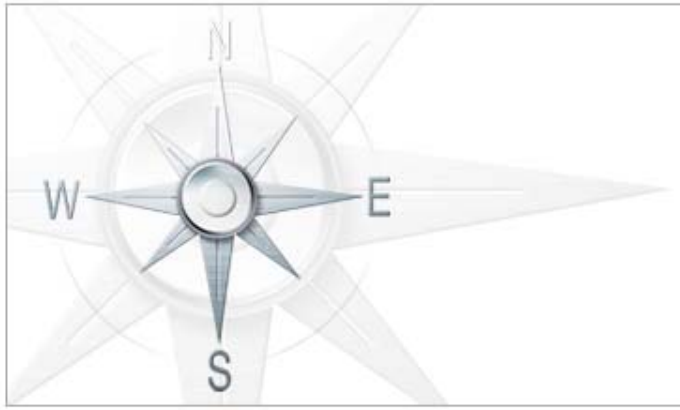


2008年中国科大

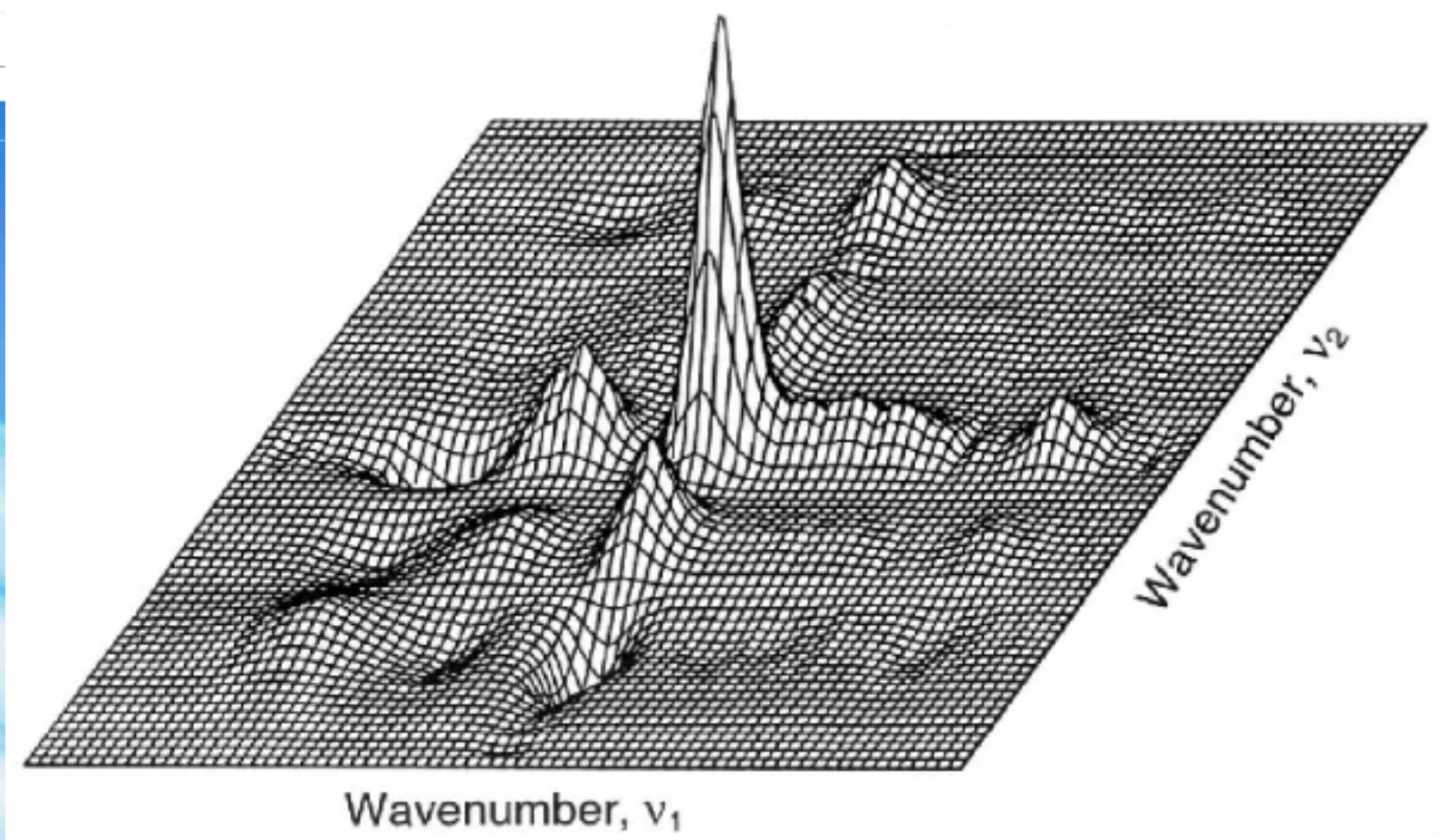
Two-Dimensional (2D) Correlation Spectroscopy

武培怡

复旦大学高分子科学系

2008-12-7

Two-Dimensional (2D) Spectroscopy



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Generalized 2D Correlation Spectroscopy

- *Generally applicable* to a broad range of spectroscopic techniques
- Based on a set of spectral data from a system under some *perturbation*
- Either *time-dependent* or *static* spectra may be used
- Enhance *spectral resolution* by spreading peaks along the second dimension
- Selective development of 2D peaks provides *better access to information* not readily observable in conventional 1D spectra
- Sign of cross peaks to determine *relative direction* of intensity changes and *sequential order* of events
- Comparison of different spectral data via *hetero-correlation*

Generalized 2D Correlation Spectroscopy

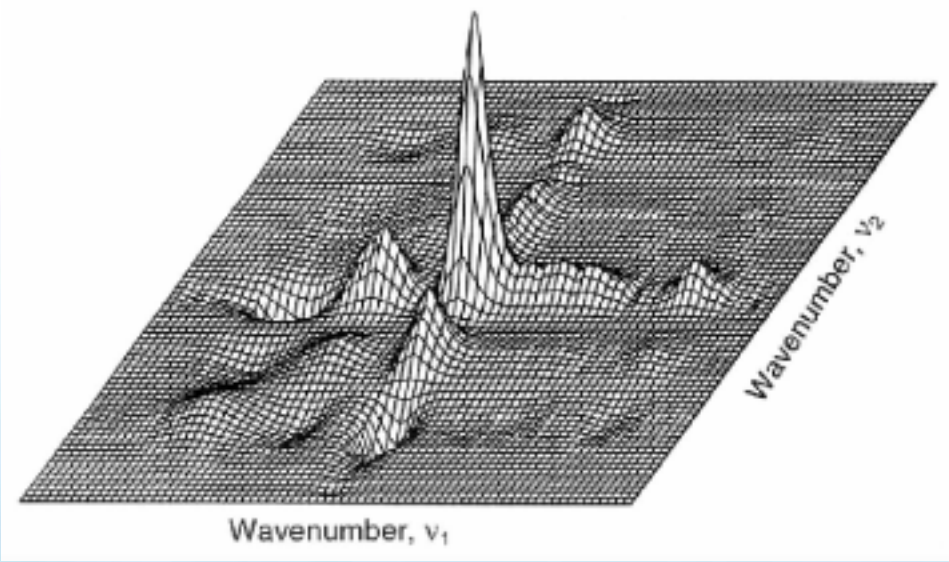
Generalized Two-Dimensional Correlation Method Applicable to Infrared, Raman, and Other Types of Spectroscopy

I. NODA

INTRODUCTION

BACKGROUND

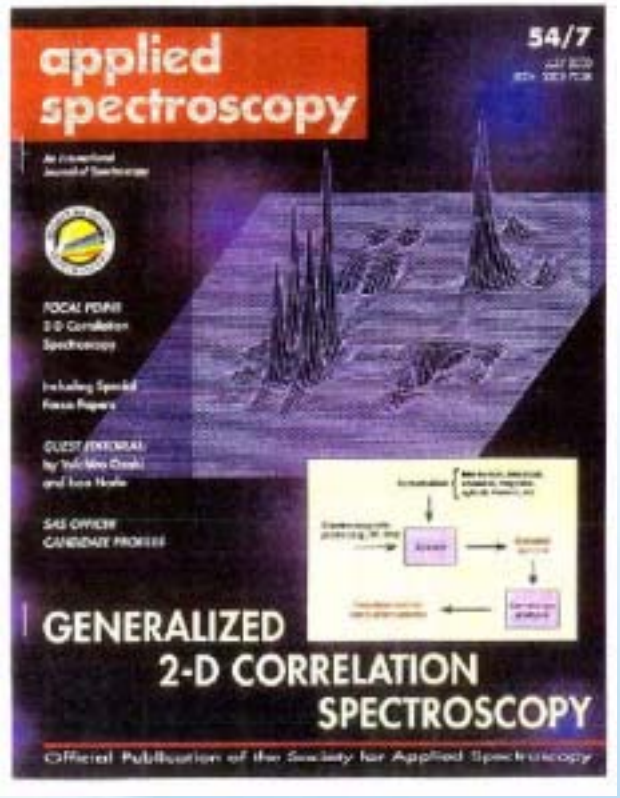
Volume 47, Number 9, 1993 APPLIED SPECTROSCOPY 1329



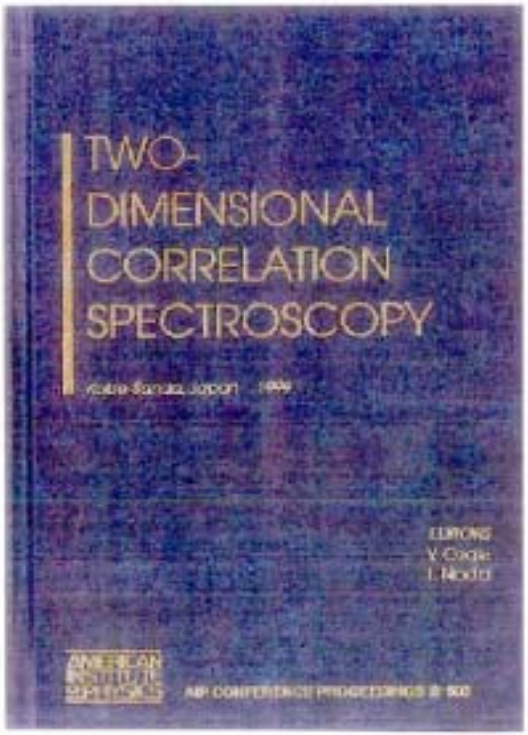
Perturbation-based 2D correlation spectroscopy

I. Noda, *Appl. Spectrosc.*, **47**, 1329 (1993).

Reference Literature



Applied Spectroscopy, vol. **54**, no. 7, July, 2000. (Special issue on generalized 2D correlation spectroscopy)



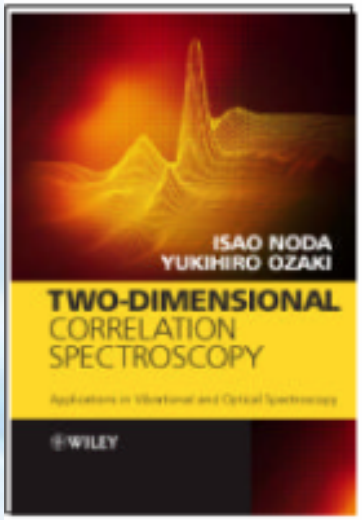
Y. Ozaki and I. Noda, Eds. Two-Dimensional Correlation Spectroscopy, AIP Conference proceedings **503**, AIP: Melville, 2000.

Book

Two-Dimensional Correlation Spectroscopy

Applications in Vibrational and Optical Spectroscopy

Isao Noda, Procter and Gamble Company, Cincinnati, Ohio, USA
and **Yukihiro Ozaki**, Kwansei Gakuin University, Japan



In the last decade or so, perturbation-based generalized two-dimensional (2D) correlation spectroscopy has become a powerful and versatile tool for the detailed analysis of various spectroscopic data. This seemingly straightforward idea of spreading the spectral information onto the second dimension, by applying the well-established classical correlation analysis methodology, has turned out to be very fertile ground for the development a new generation of modern spectral analysis techniques.

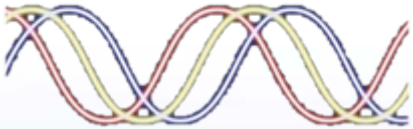
This book is a valuable tool for individuals using correlation spectroscopy and those who want to start using this technique. Written by two of the biggest names in the field – Isao Noda is the founder of this technique – this is the first book on 2D vibrational and optical spectroscopy available in one single source.

This book serves as an introductory text for newcomers to the field, as well as presents a survey of specific interest areas for the experienced practitioner.

Generalized Two-Dimensional Correlation Spectroscopy

Electromagnetic Probe

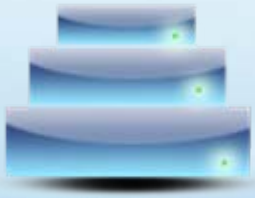
IR, NIR, laser ……



Chemical System

Dynamic Spectra

External Perturbation



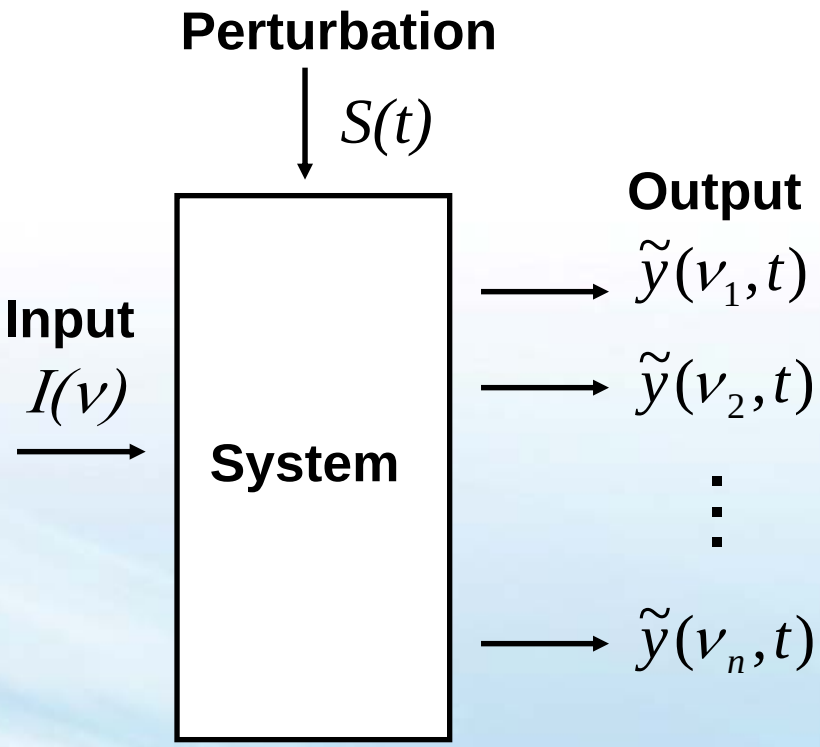
Temperature, pressure, time, concentration, electromagnetic field ……

2D Correlation Spectra

Acquisition of 2D Correlation Spectra

7

2D Correlation Analysis



Comparison of two signals measured at different ν along ***t***

Cross-correlation function

$$X(\nu_1,\nu_2) = \langle \tilde{y}(\nu_1,t) \cdot \tilde{y}(\nu_2,t') \rangle$$
$$= \Phi(\nu_1,\nu_2) + i\,\Psi(\nu_1,\nu_2)$$

Synchronous spectrum

$\Phi(\nu_1,\nu_2)$ = Similarity of signal dependence on ***t***

Asynchronous spectrum

$\Psi(\nu_1,\nu_2)$ = Dissimilarity of signal dependence on ***t***

Generalized 2D Correlation Formalism

Dynamic spectrum

$$\tilde{y}(\nu,t) = \begin{cases} y(\nu,t) - \bar{y}(\nu) & \text{for} \quad T_{\min} \le t \le T_{\max} \\ 0 & \text{otherwise} \end{cases}$$

$$\text{where} \quad \bar{y}(\nu) = \frac{1}{T_{\max} - T_{\min}} \int_{T_{\min}}^{T_{\max}} y(\nu,t)\,dt.$$

Fourier transform

$$\tilde{Y}_1(\omega) = \int_{-\infty}^{\infty} \tilde{y}(\nu_1,t)\; e^{-i\omega t} dt$$

$$\tilde{Y}_2^{*}(\omega) = \int_{-\infty}^{\infty} \tilde{y}(\nu_2,t)\; e^{+i\omega t} dt$$

2D correlation spectra

$$\Phi(\nu_1,\nu_2) + i\,\Psi(\nu_1,\nu_2) = \frac{1}{\pi\,(T_{\max} - T_{\min})} \int_0^{\infty} \tilde{Y}_1(\omega) \cdot \tilde{Y}_2^{*}(\omega)\, d\omega$$

$\Phi(\nu_1, \nu_2) =$ synchronous spectrum

$\Psi(\nu_1, \nu_2) =$ asynchronous spectrum

Practical Computational Method

Discrete spectral sampling

$$\tilde{y}_j(\nu) = \begin{cases} y_j(\nu) - \bar{y}(\nu) & for \quad 1 \le j \le m \\ 0 & otherwise \end{cases} \qquad \bar{y}(\nu) = \frac{1}{m}\sum_{j=1}^{m} y_j(\nu)$$

Discrete Hilbert transform

$$\tilde{z}_j(\nu_2) = \sum_{k=1}^{m} N_{jk} \cdot \tilde{y}_k(\nu_2) \qquad where \qquad N_{jk} = \begin{cases} 0 & if \quad j = k \\ 1/\pi(k-j) & otherwise \end{cases}$$

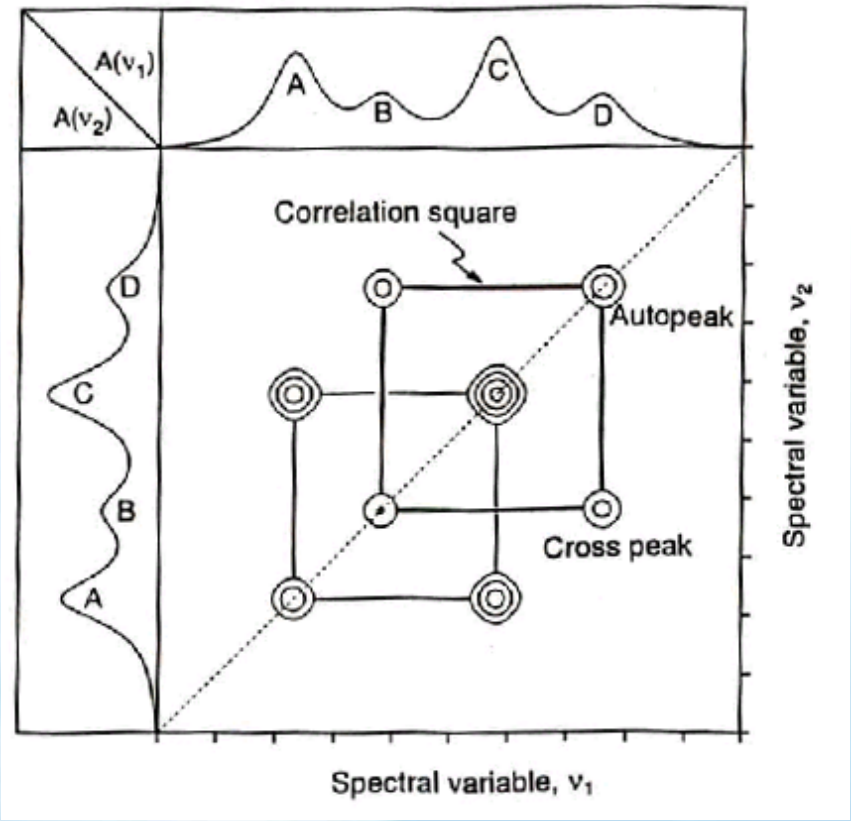
2D correlation spectra

$$\Phi(\nu_1, \nu_2) = \frac{1}{m-1}\sum_{j=1}^{m} \tilde{y}_j(\nu_1) \cdot \tilde{y}_j(\nu_2)$$

$$\Psi(\nu_1, \nu_2) = \frac{1}{m-1}\sum_{j=1}^{m} \tilde{y}_j(\nu_1) \cdot \tilde{z}_j(\nu_2)$$

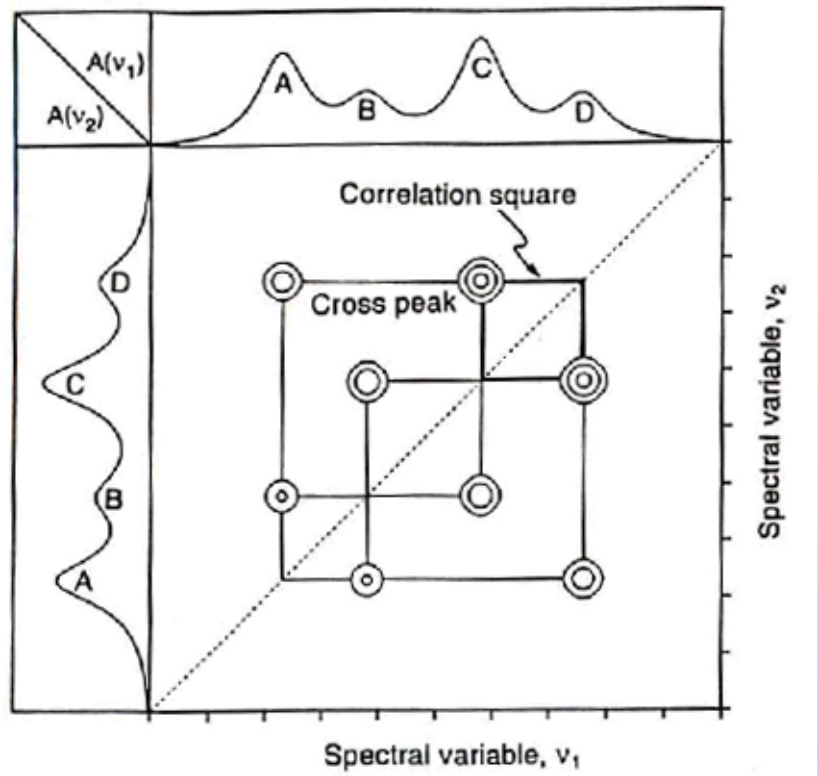
Rapid and straightforward computation of 2D correlation spectra

Synchronous correlation spectrum: $\Phi(\nu_1, \nu_2)$



- **Autopeaks** at diagonal positions represent the **extent** of perturbation-induced dynamic fluctuations of spectral signals
- **Cross peaks** represent **simultaneous changes** of spectral signals at two different wavenumbers, suggesting a coupled or related origin of intensity variations
- If the **sign** of a cross peak is **positive**, the intensities at corresponding wavenumbers are increasing (or decreasing) together. If the sign is **negative**, one is increasing, while the other is decreasing.

Asynchronous correlation spectrum: $\Psi(\nu_1, \nu_2)$



- **Cross peaks** develop only if the intensity varies **out of phase** with each other for some Fourier frequency components of signal fluctuations
- The **sign** of a cross peak is **positive** if the intensity change at ν_1 occurs before ν_2.
- The **sign** of a cross peak is **negative** if the intensity change at ν_1 occurs after ν_2.
- The above sign rules are reversed if $\Phi(\nu_1, \nu_2)<0$.

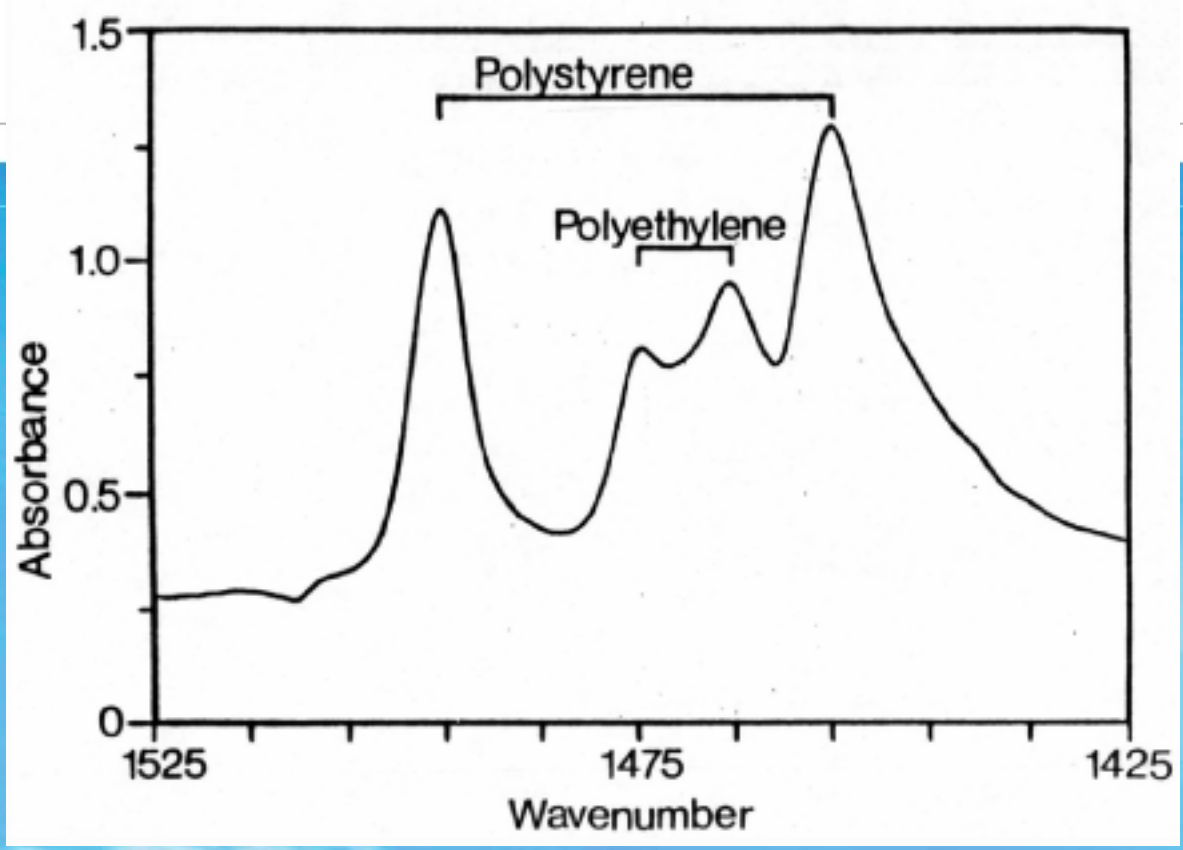
Polystyrene/Polyethylene Blend

Polystyrene

$-(CH_2CH)_n-$

Polyethylene

$-(CH_2CH_2)_n-$



- PS and PE are immiscible (phase separated)
- No molecular level interactions

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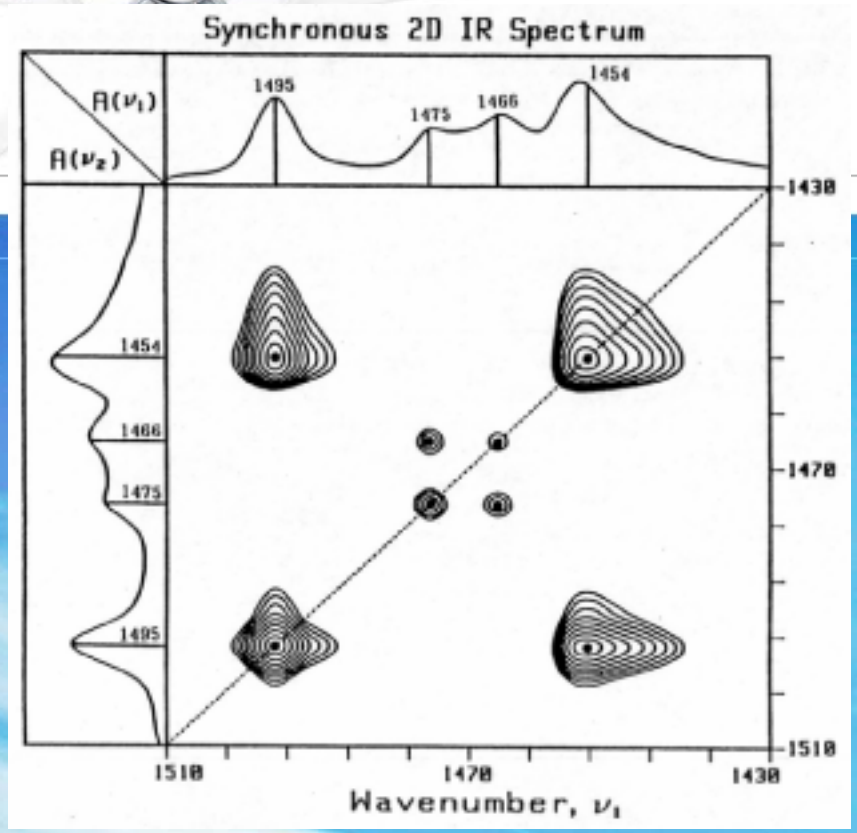
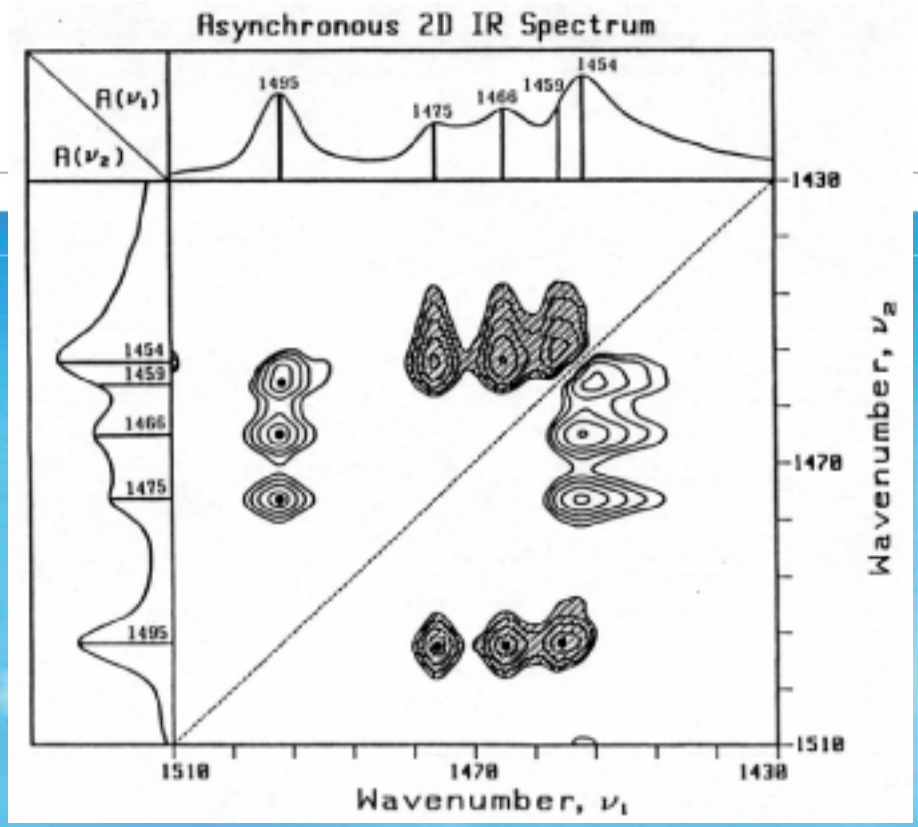
Polystyrene/Polyethylene Blend





- Separate synchronous correlations for PS and PE bands
- Asynchronous correlation between PS and PPE bands
- Asynchronicity within PS bands (backbone vs. side group)

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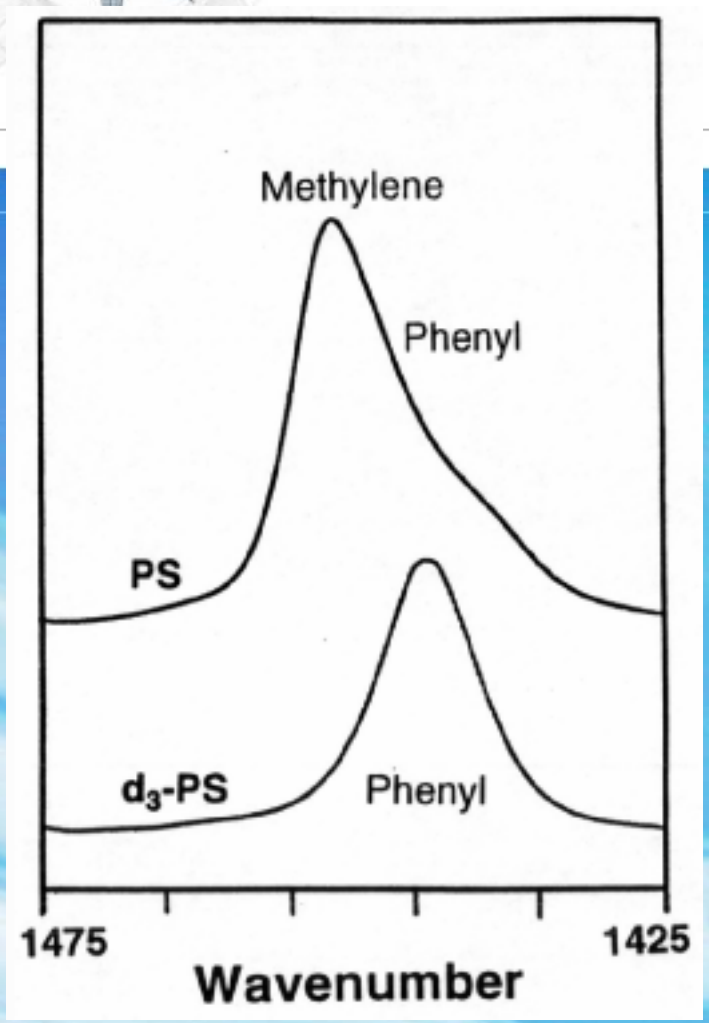
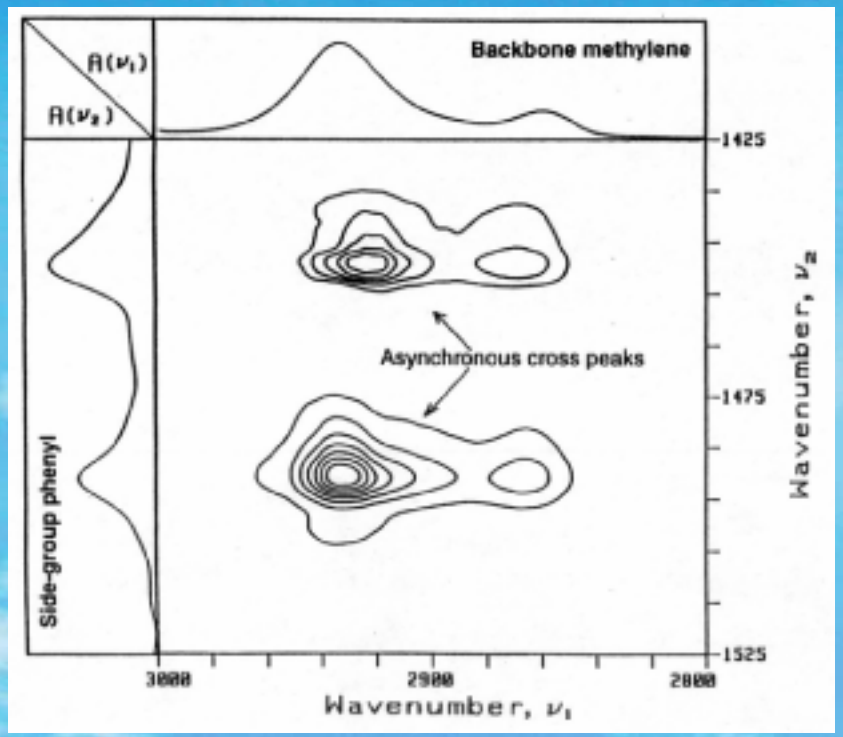
Selectively Deuterated Polystyrene



$-(CH_2CH)_n-$ *vs.* $-(CD_2CD)_n-$



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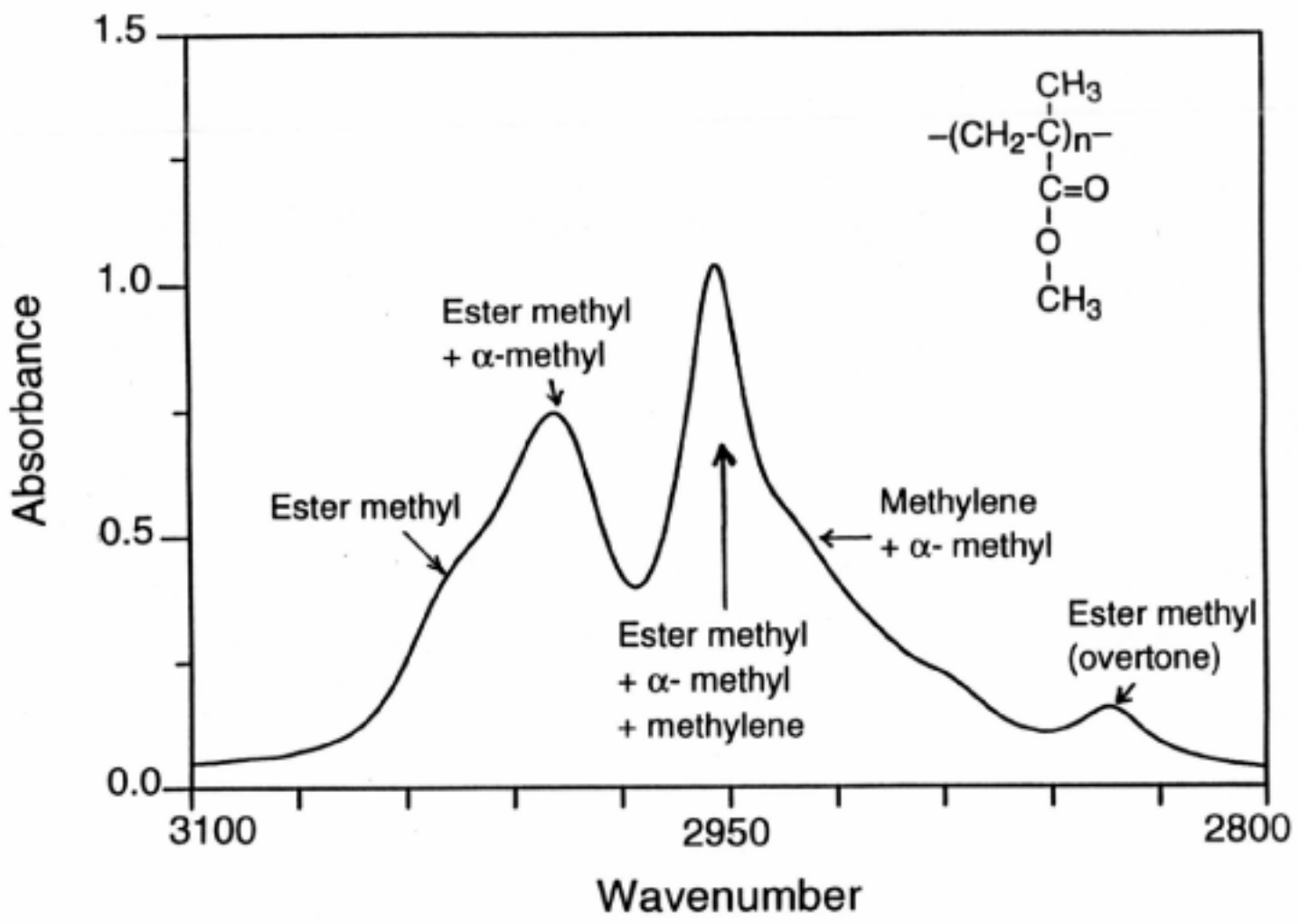
Atactic Poly(methyl methacrylate)



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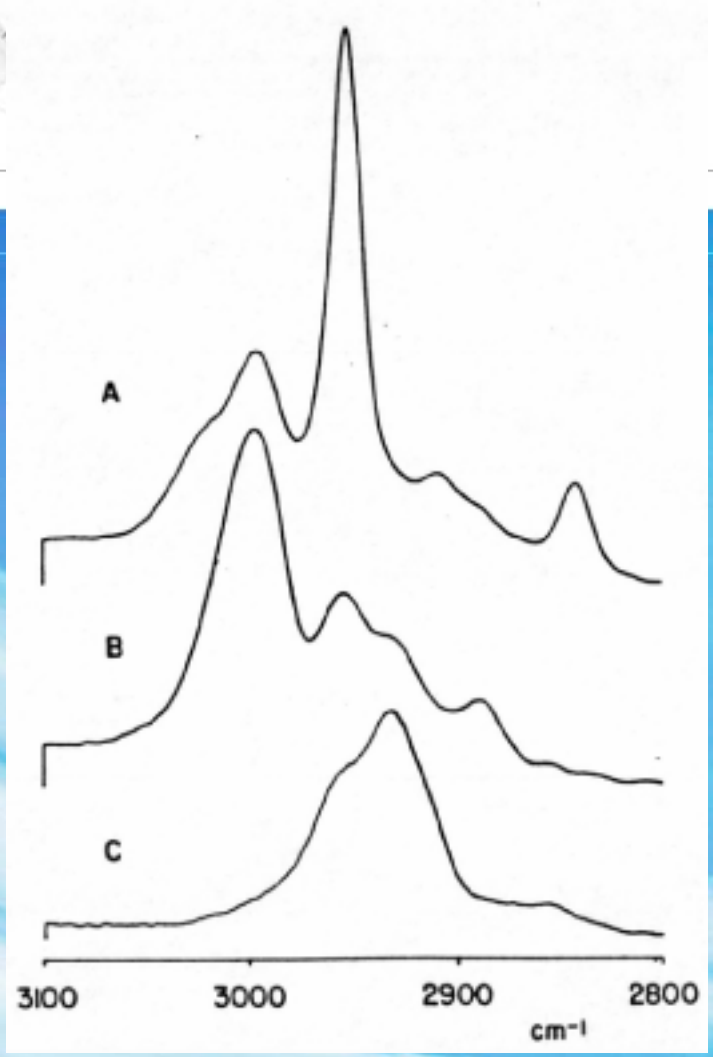
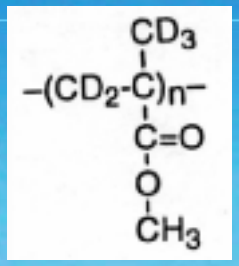
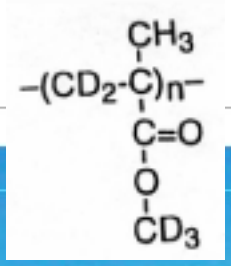
Pure Group Frequency Spectra of PMMA

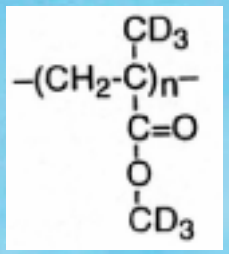




A. Ester methyl



B. Alpha methyl

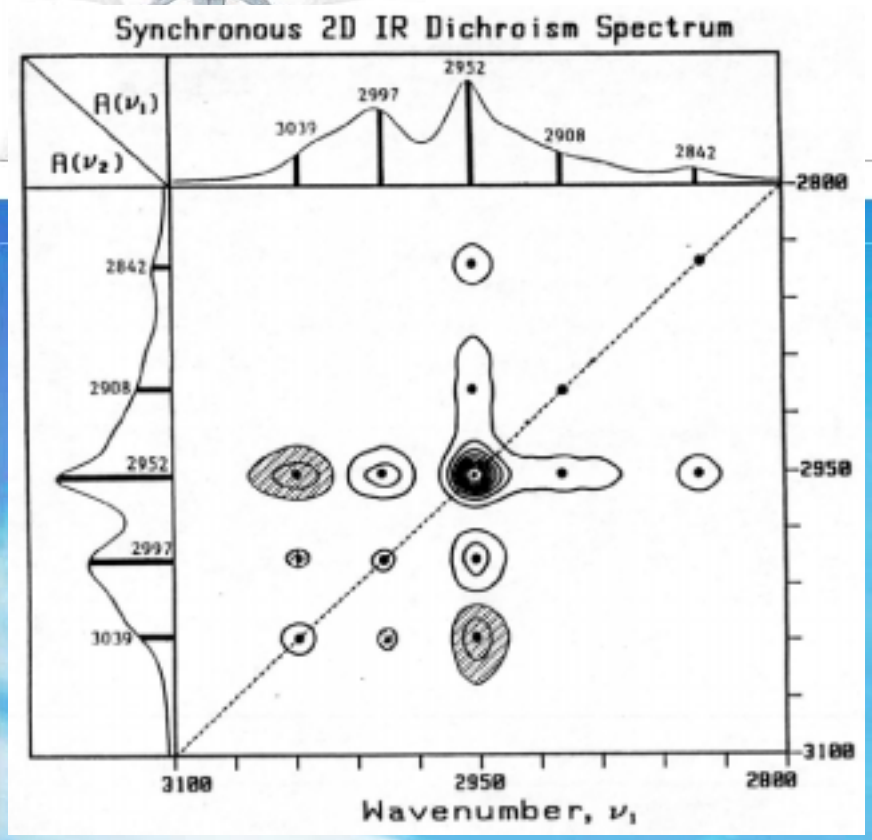


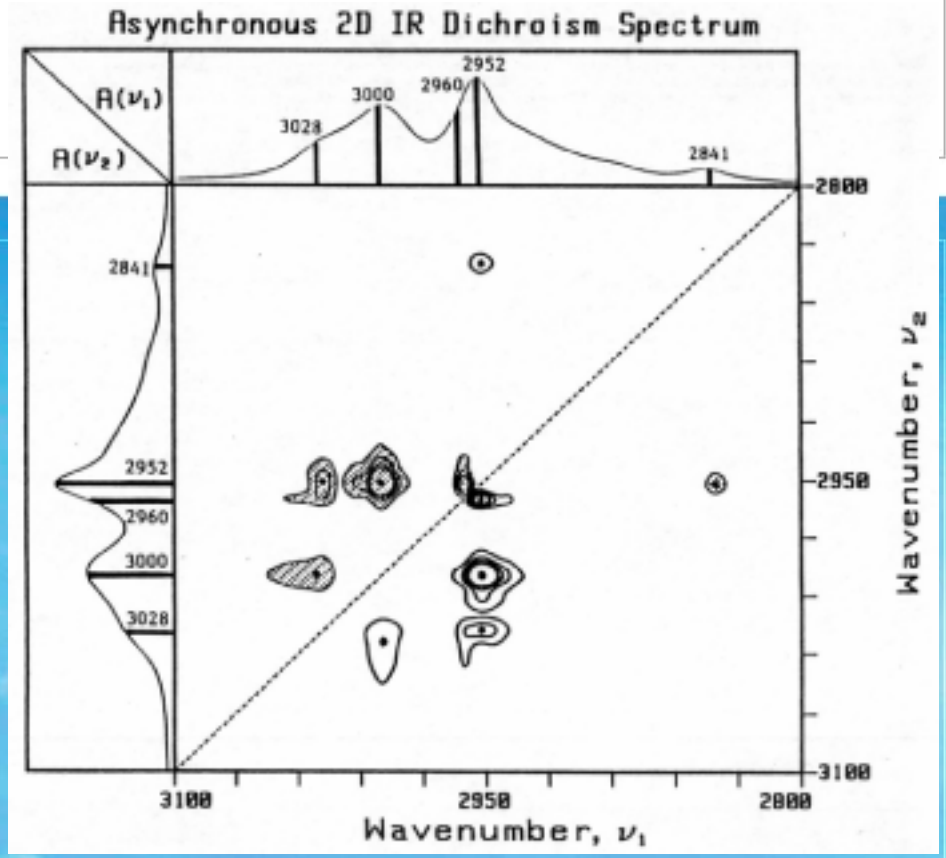
C. Methylene

S.K. Dirlikov and J.L. Koenig
Appl. Spectrosc. 33, 555 (1979).

2008-12-7

Atactic PMMA





- Ester methyl peaks are in the synchronous spectrum almost exclusively
- Alpha methyl and methylene found in the asynchronous spectrum

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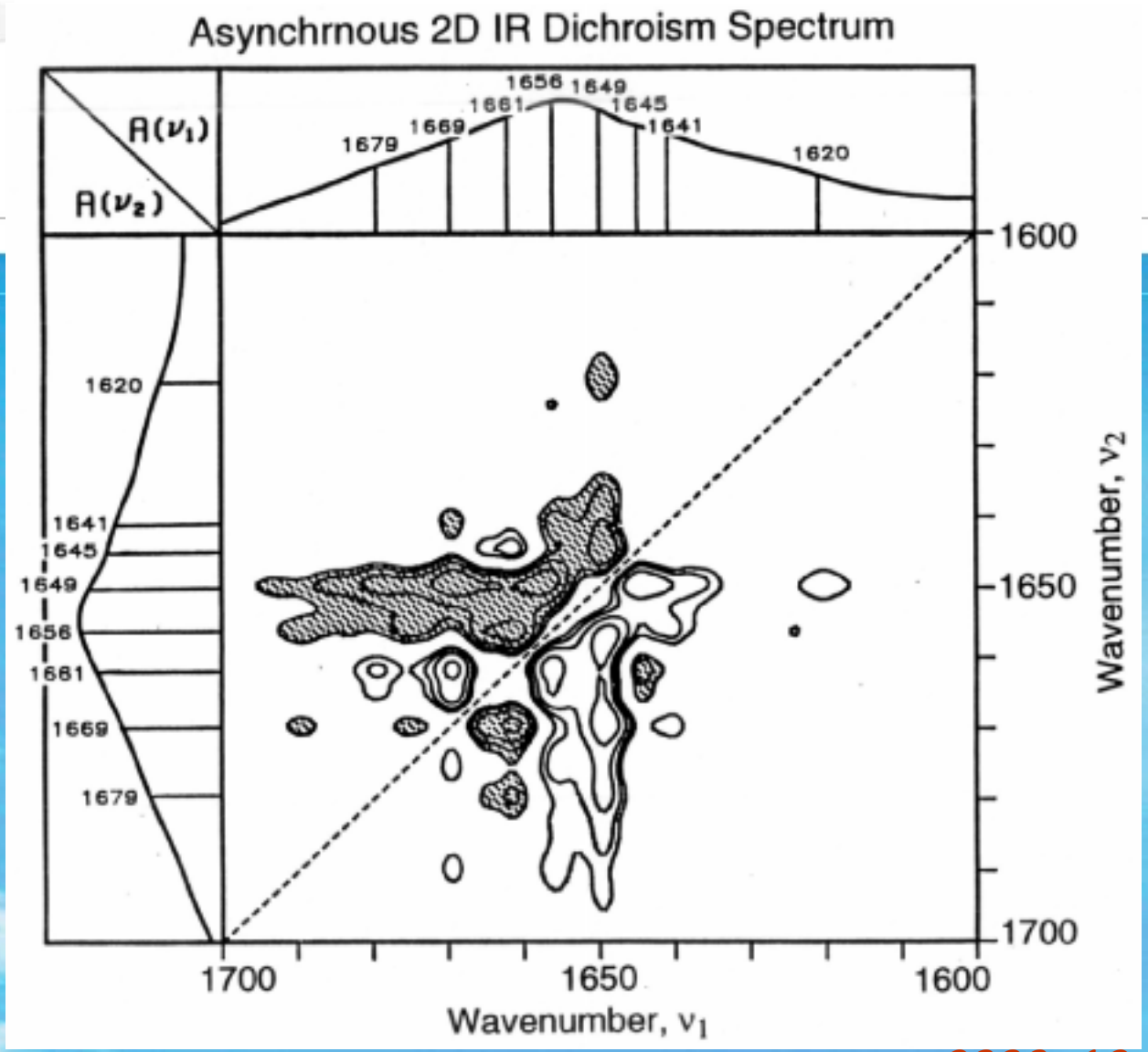
Human Hair Keratin

Assignments (cm^{-1})

α-helix
1661, 1649

β-like extended chains and turns
1679, 1669, 1645
1641, 1620

Disordered structures
1656



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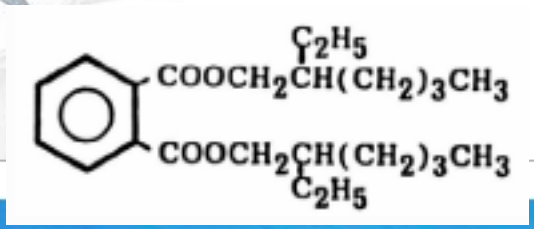
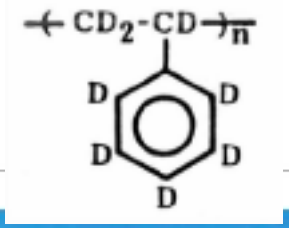
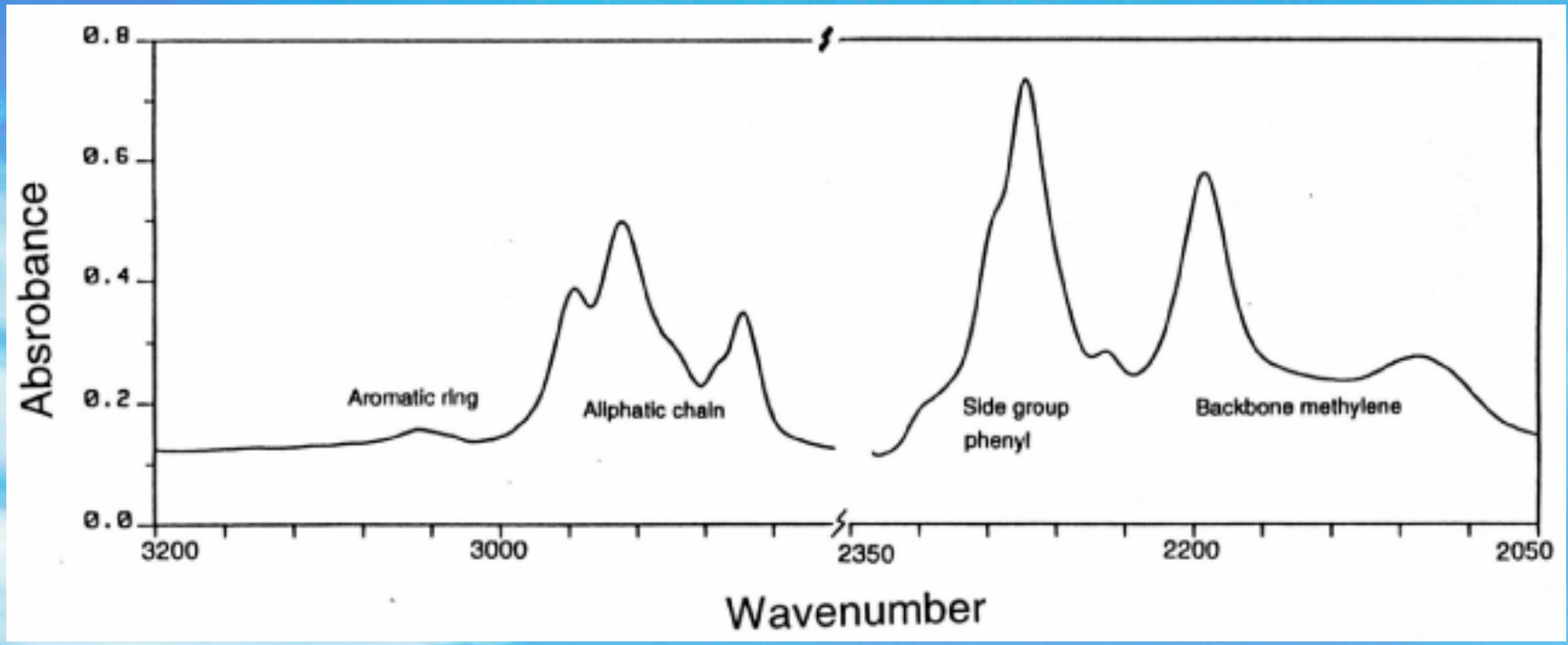
Polystyrene/DOP Blend



Dioctyl phthalate (DOP)



Perdeuterated polystyrene



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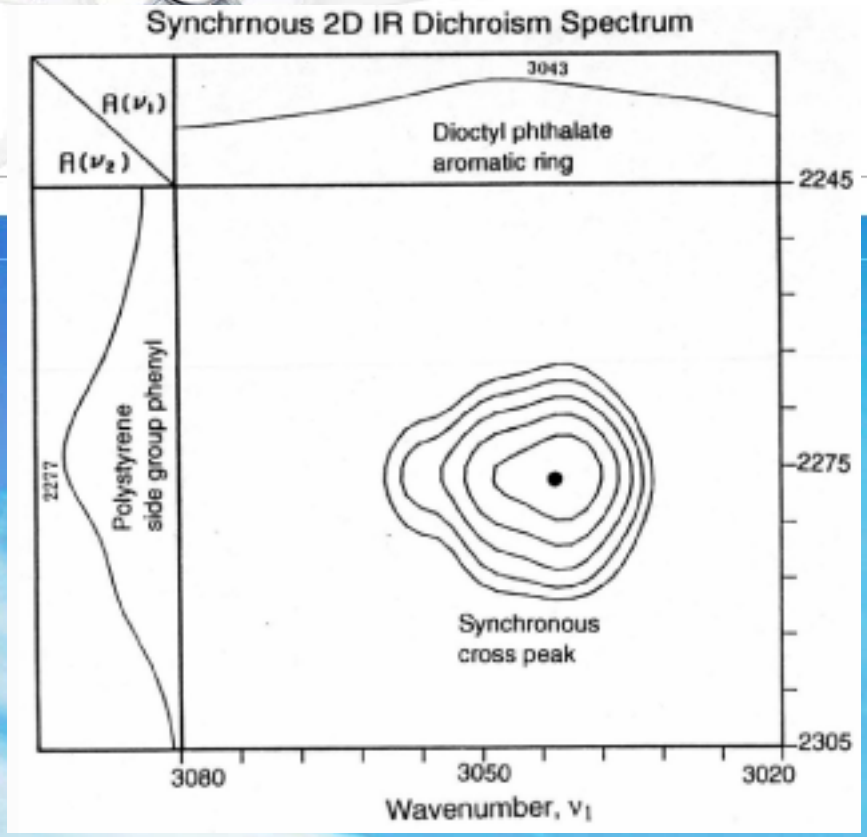
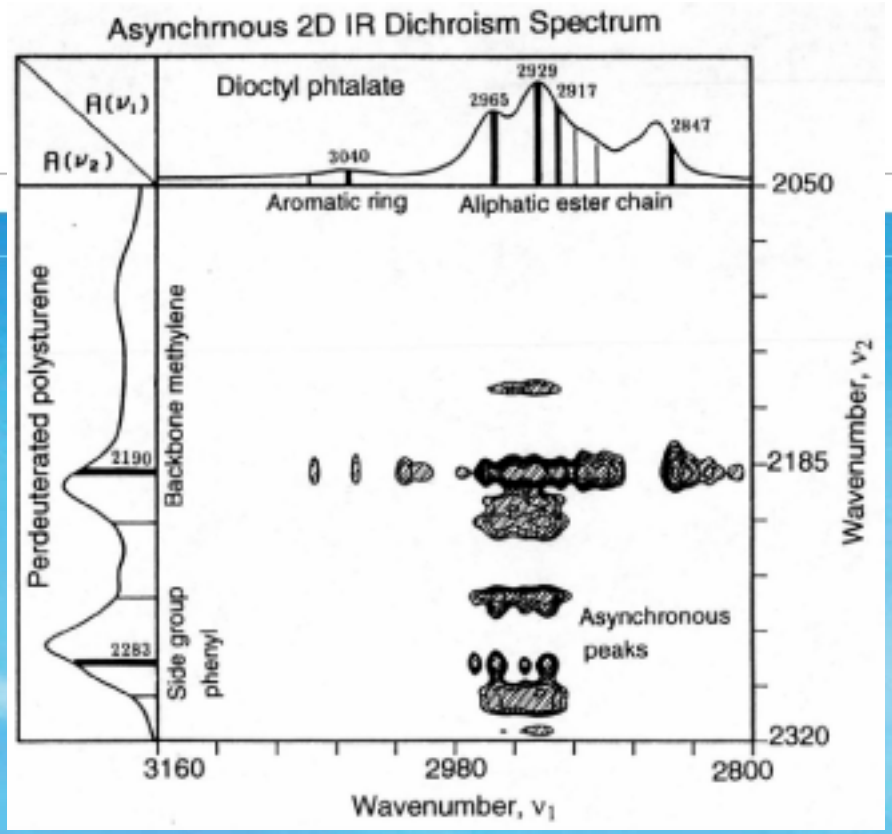
Plasticized Polystyrene





- Motions of aromatic groups of PS and DOP are synchronized
- DOP aliphatic chains move asynchronously (independently) with respect to PS phenyl rings

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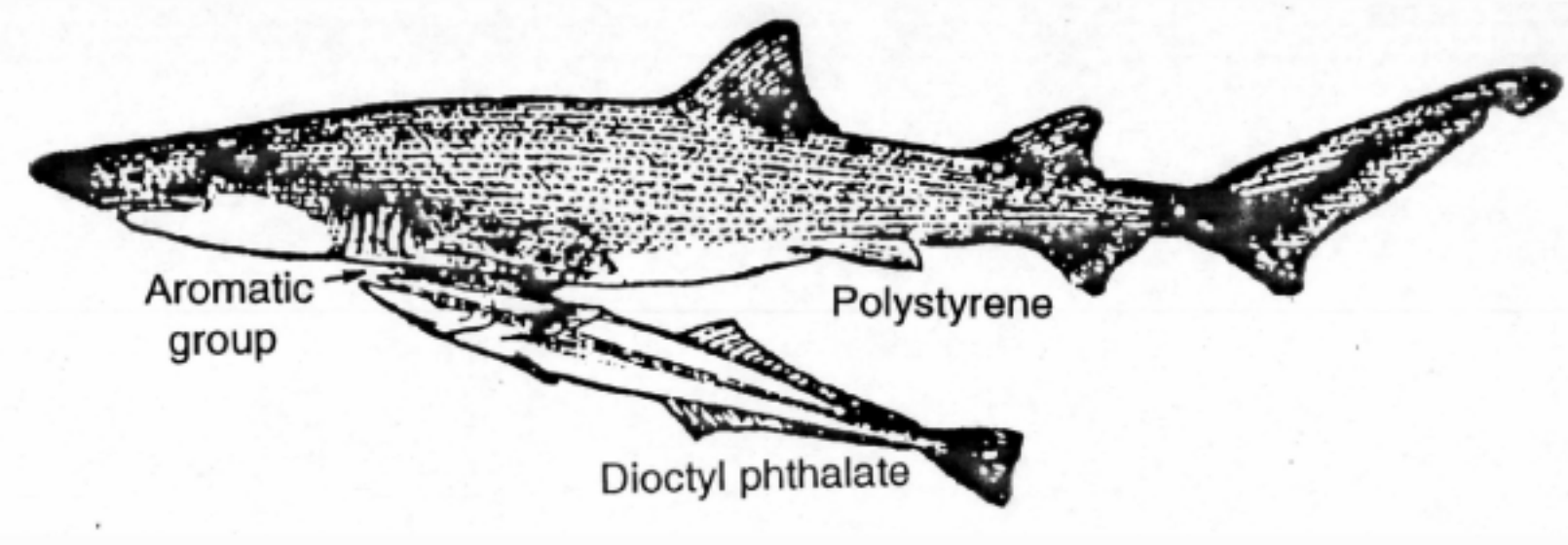
Remola Model of Plasticization



rem'o-ra, *n.* [L., hinderance.] **1.** Any of several fishes (gerera *Echenecis*, *Remora*, family Echneididae), with a suctional disk on the head by which they cling to other fishes or to ships. **2.** A clog; drags; hinderence.

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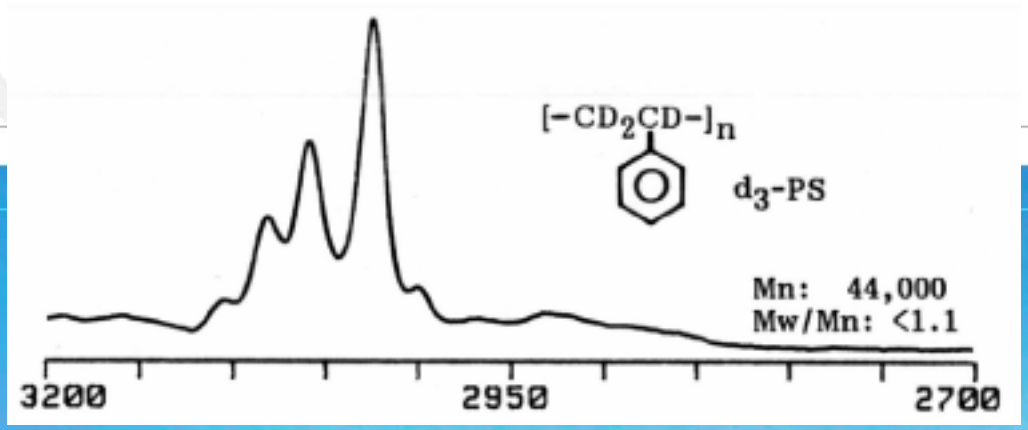
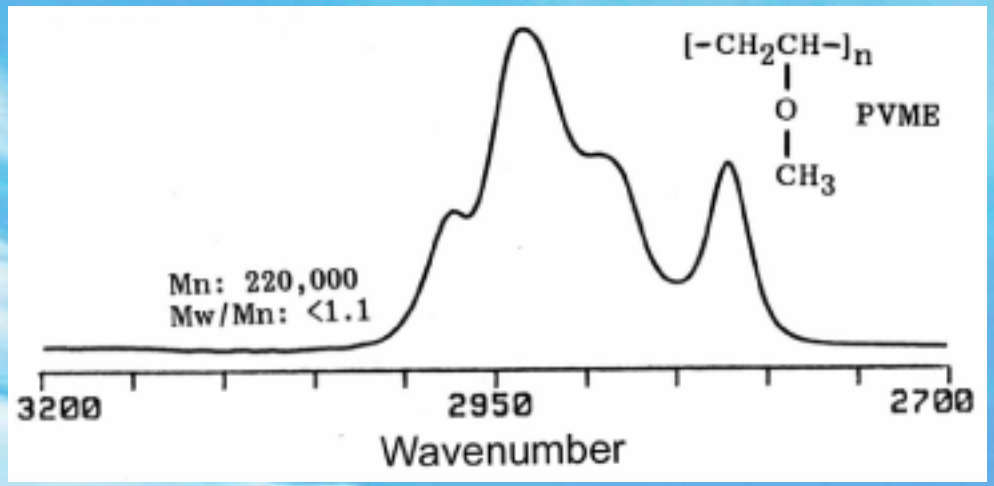
PS/PVME Blends

Polystyrene (chain-deuterated)



Poly(vinyl methyl ether)



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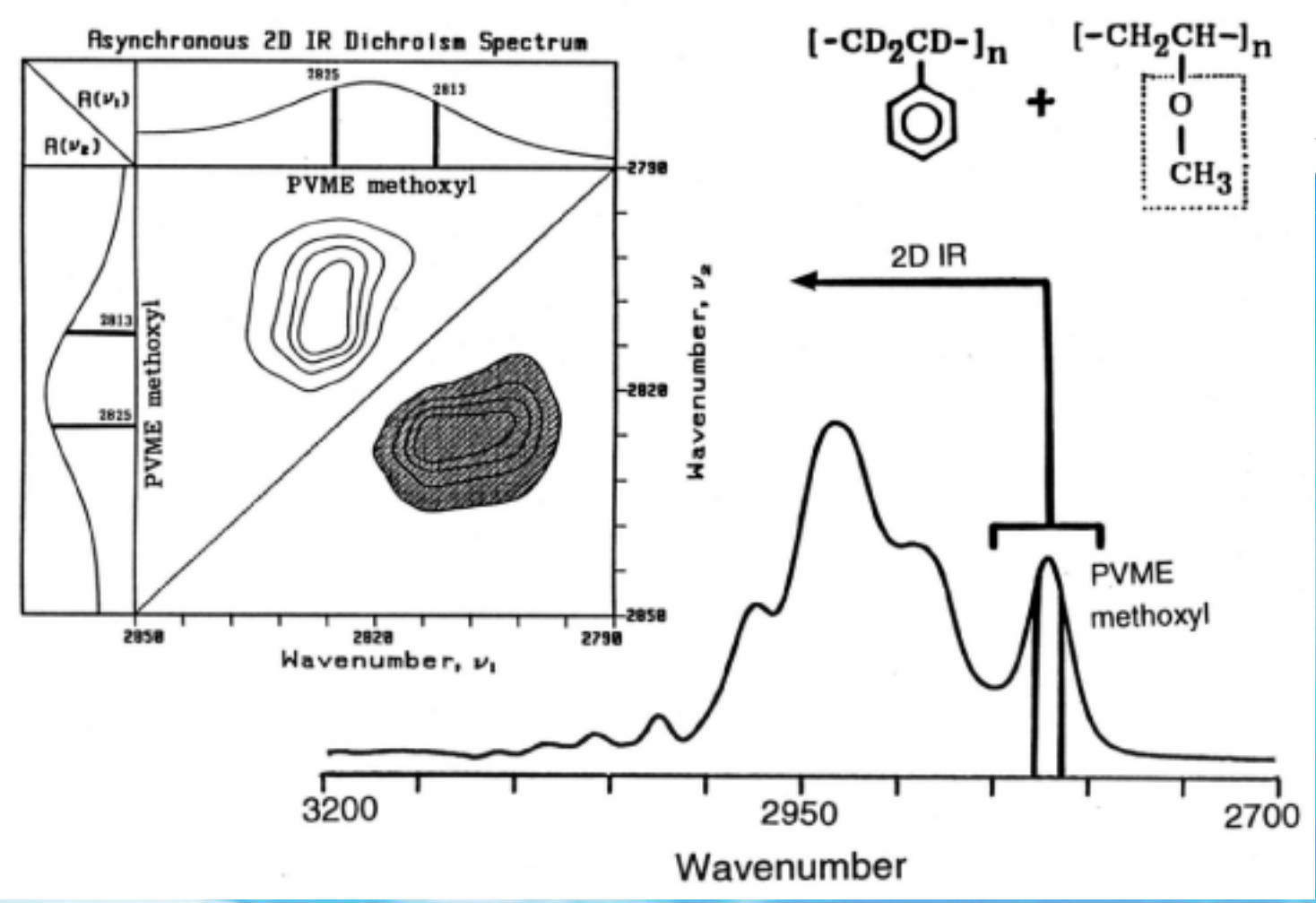
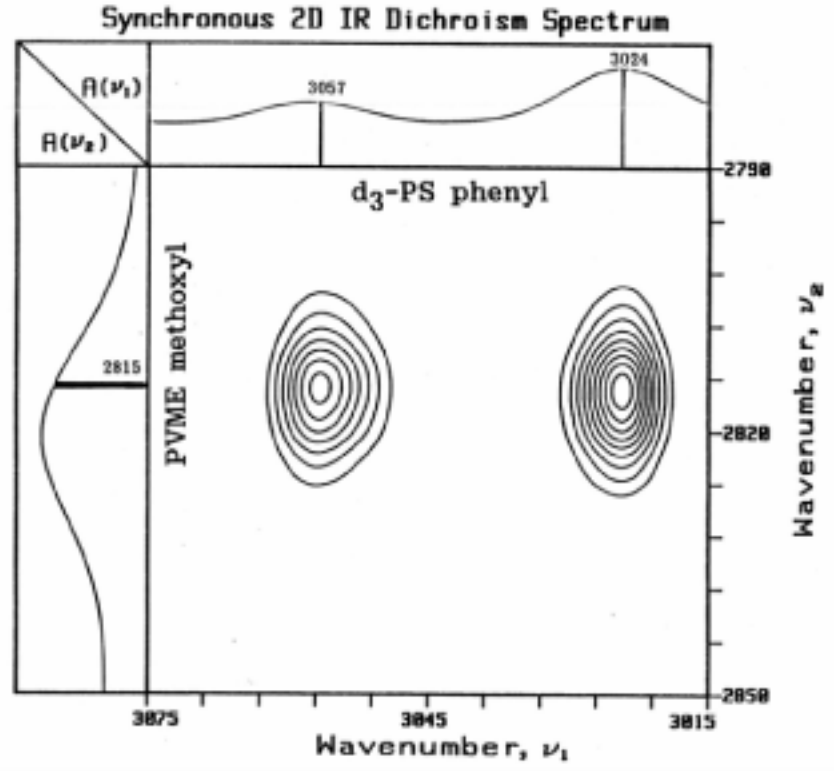
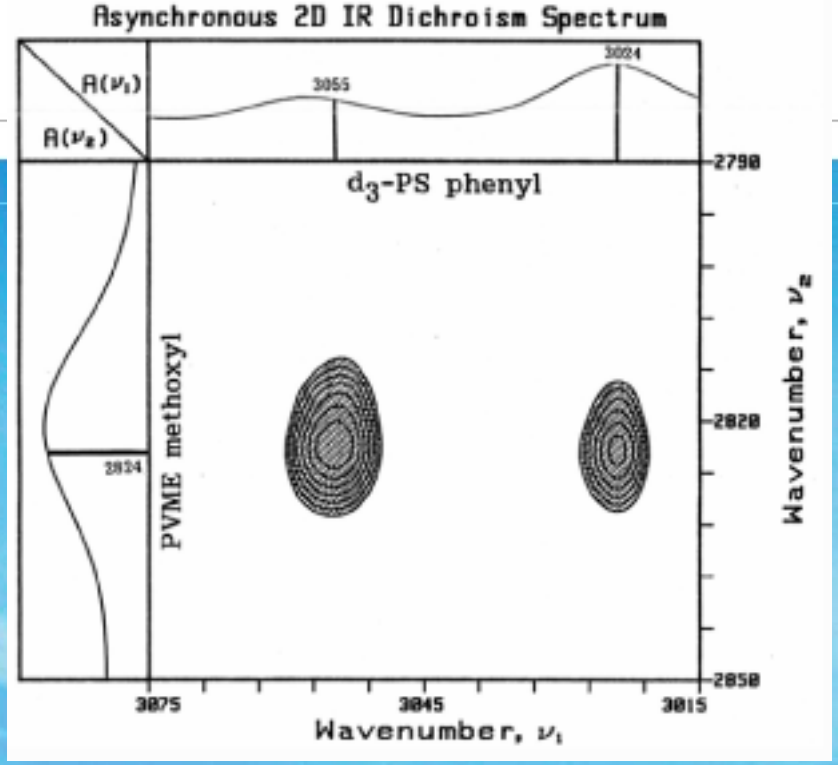
d_3PS/PVME (25:75) Blend



2008-12-7

d_3PS/PVME (25:75) Blend





- Band split of PVME methoxyl groups into 2815 cm^{-1} and 2824 cm^{-1}
- Motion of PVME 2815 cm^{-1} is synchronized with PS phenyl

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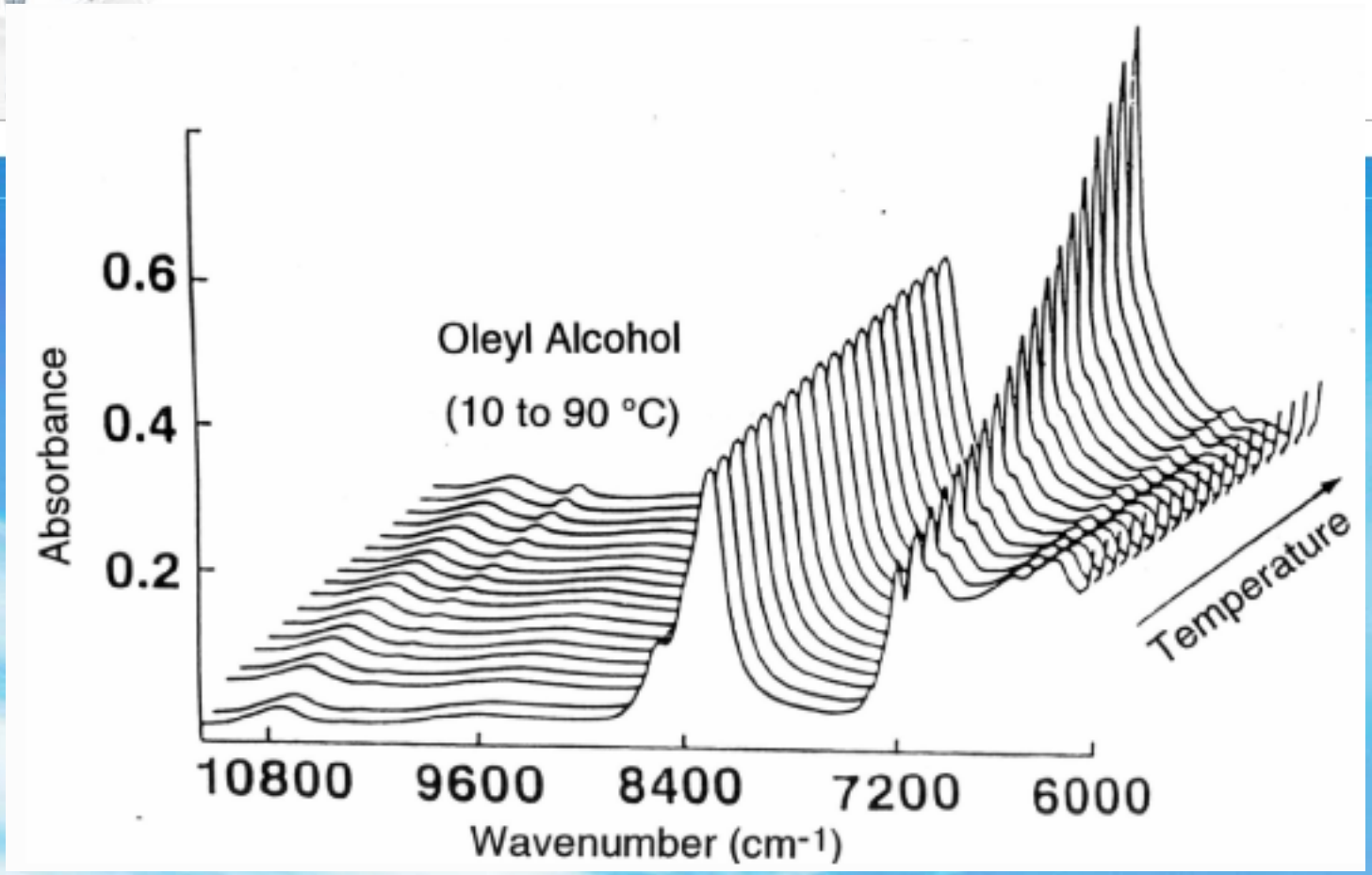
FT NIR Spectra of Oleyl Alcohol



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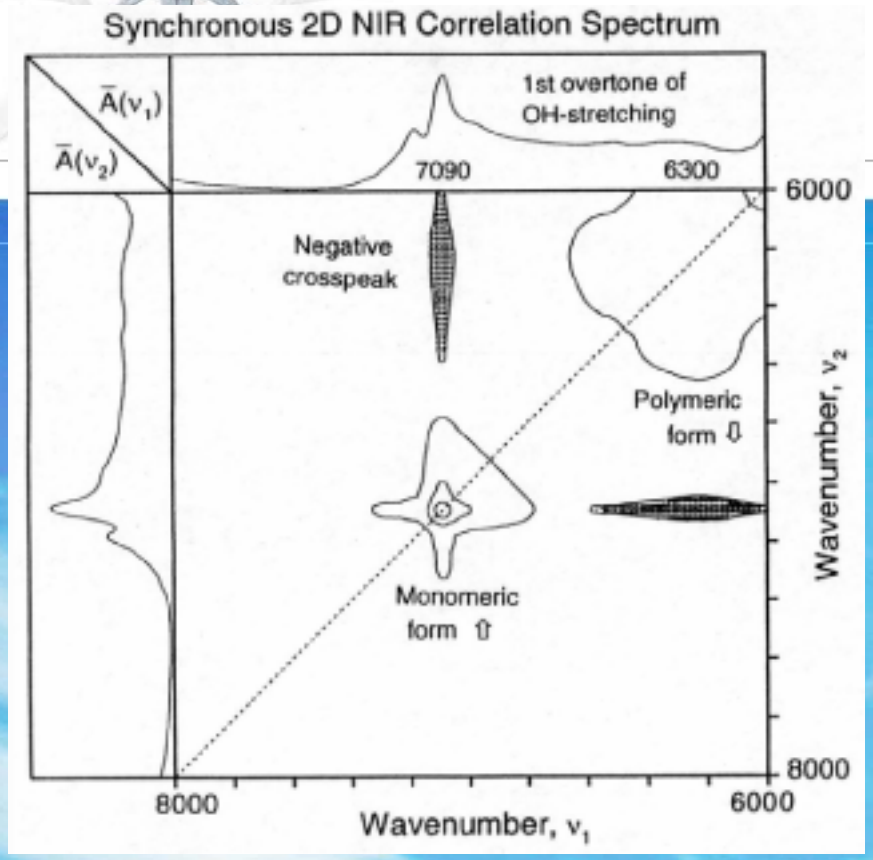
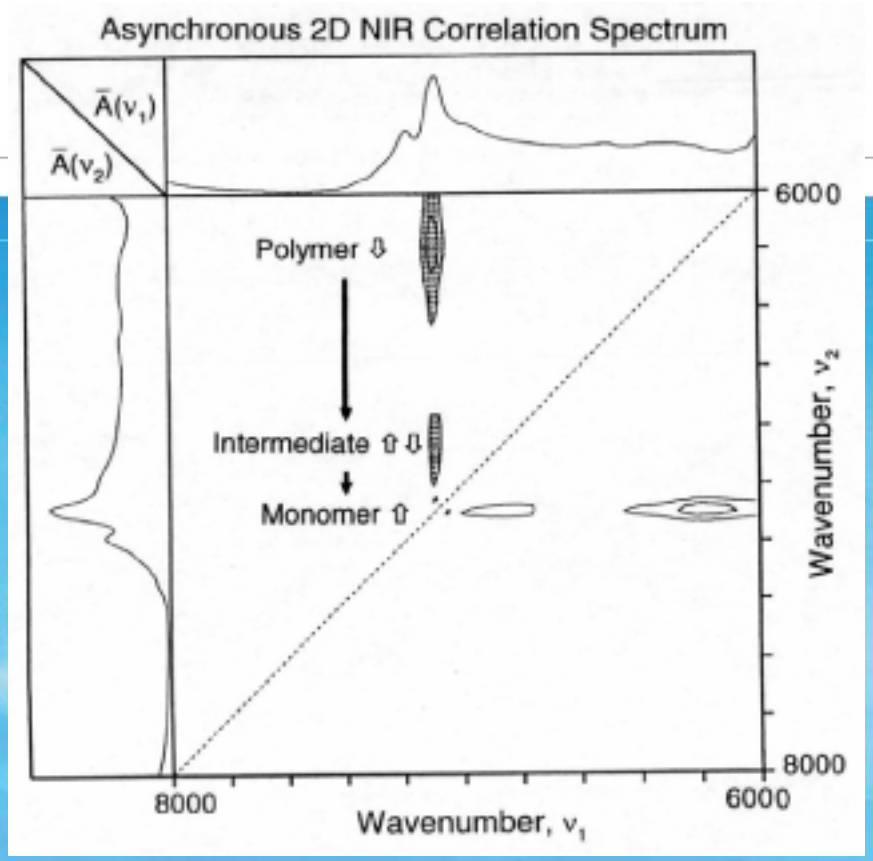
Thermal 2D NIR of Oleyl Alcohol





- Associated “polymers” decrease, as monomers increase
- Not a direct conversion (asynchronous peaks)
- Intermediate states (e.g., dimers) exist

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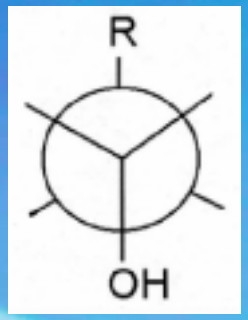
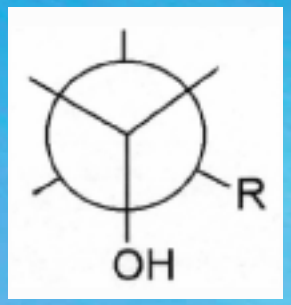
Thermal 2D NIR of Oleyl Alcohol

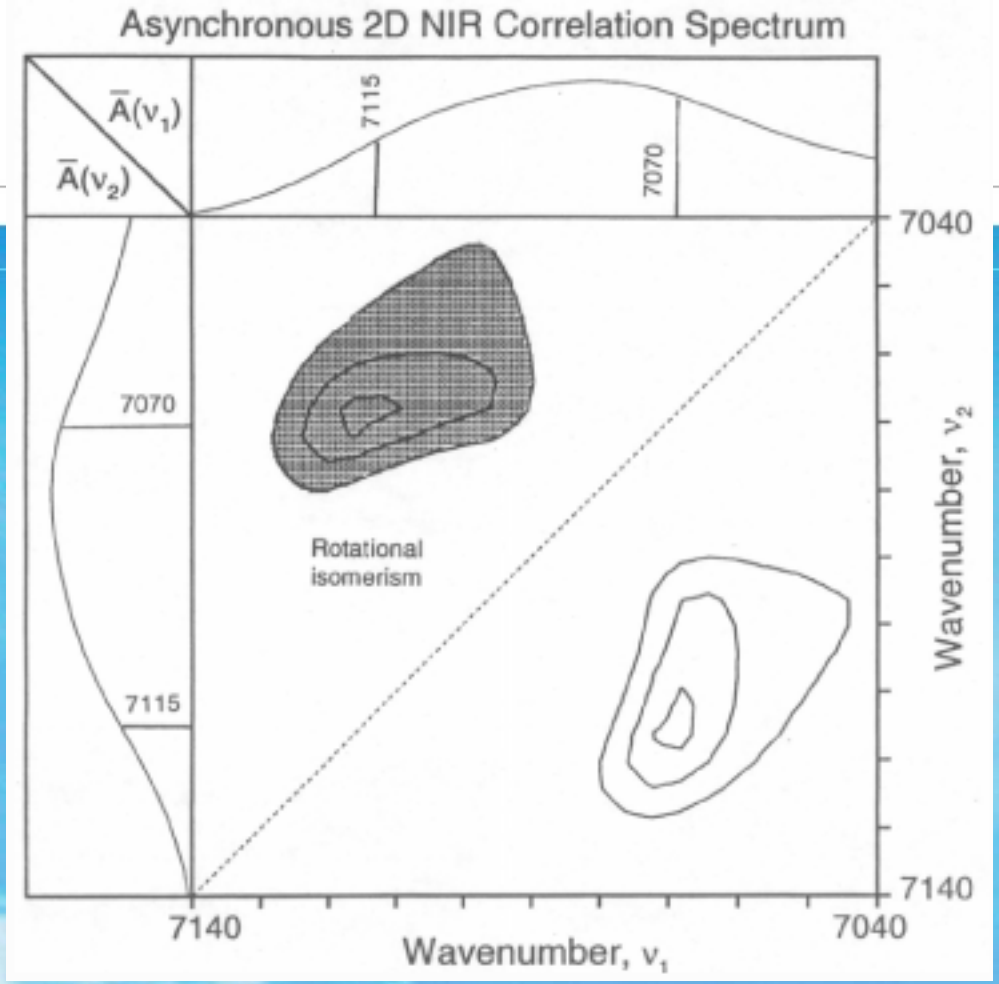
Rotational isomers



Trans

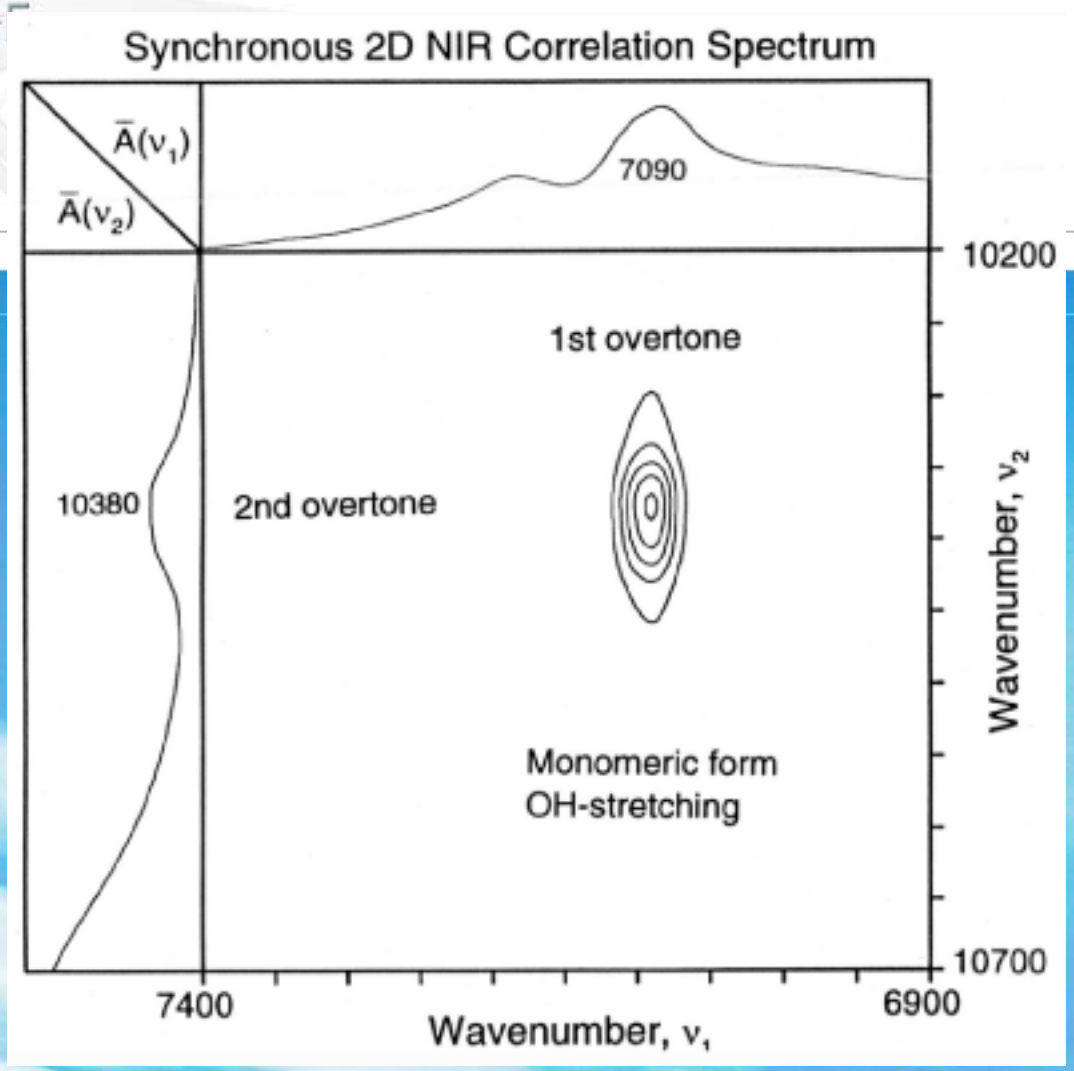


Gauche



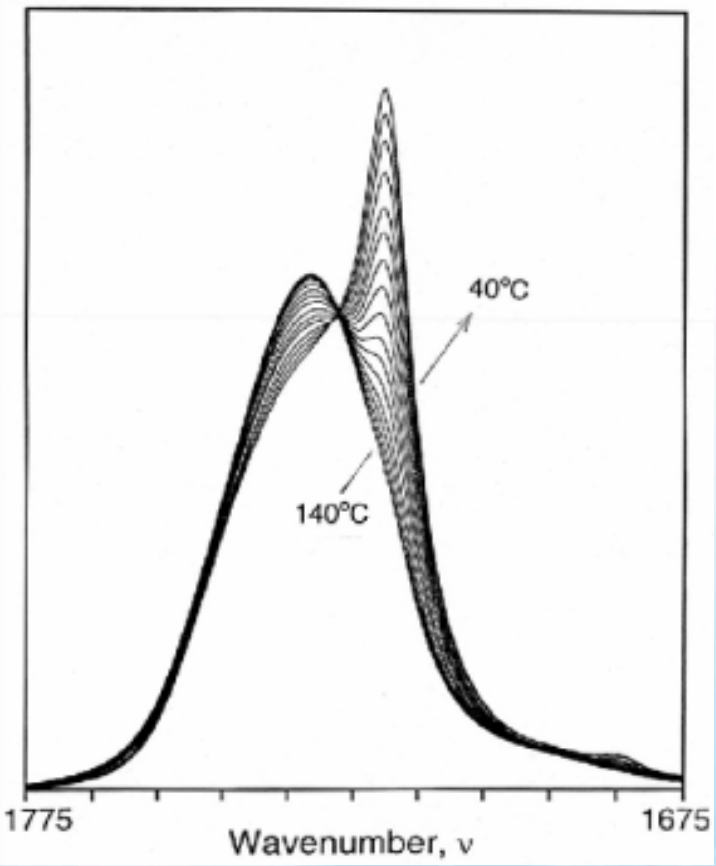
2008-12-7

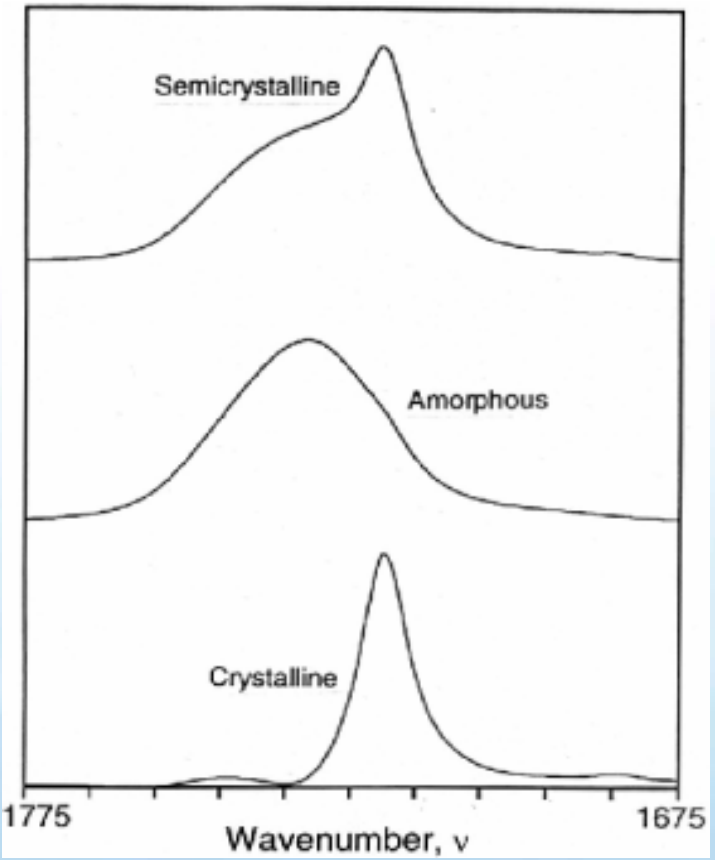
Thermal 2D NIR of Oleyl Alcohol



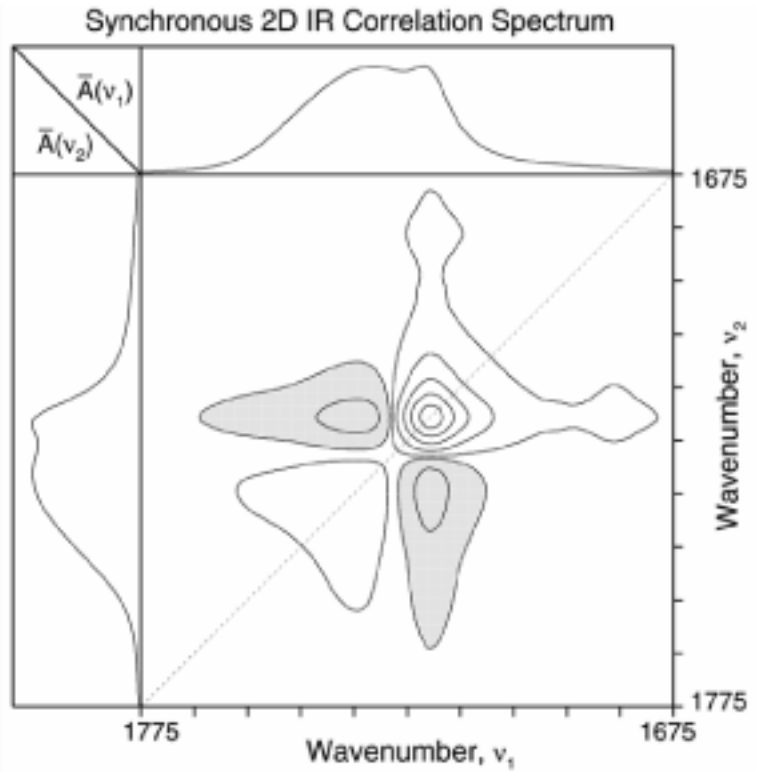
2008-12-7

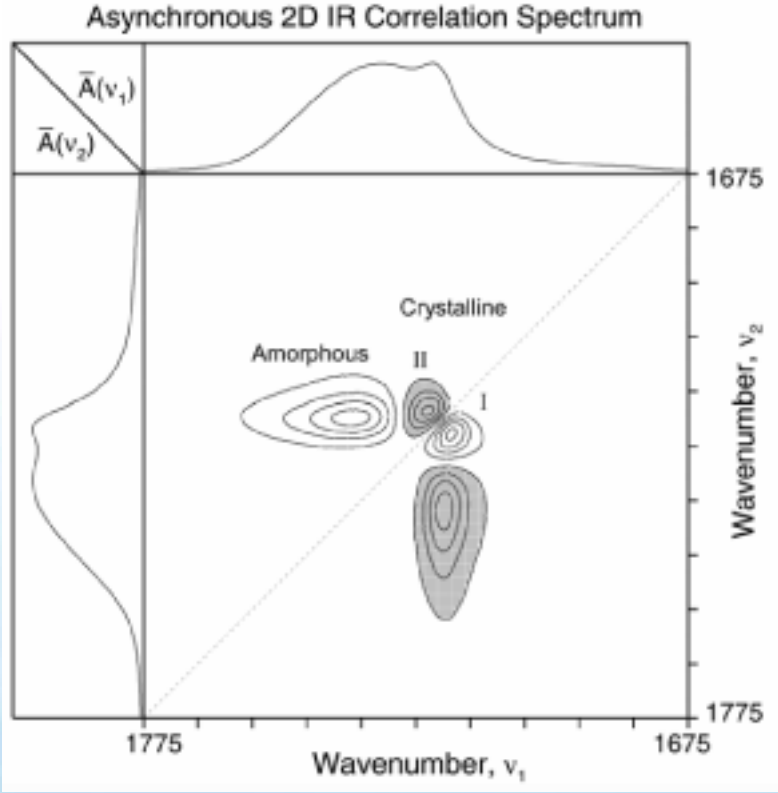
Crystallization of *Nodax*^{TM} (PHBHx)





Crystallization of *Nodax*^{TM} (PHBHx)





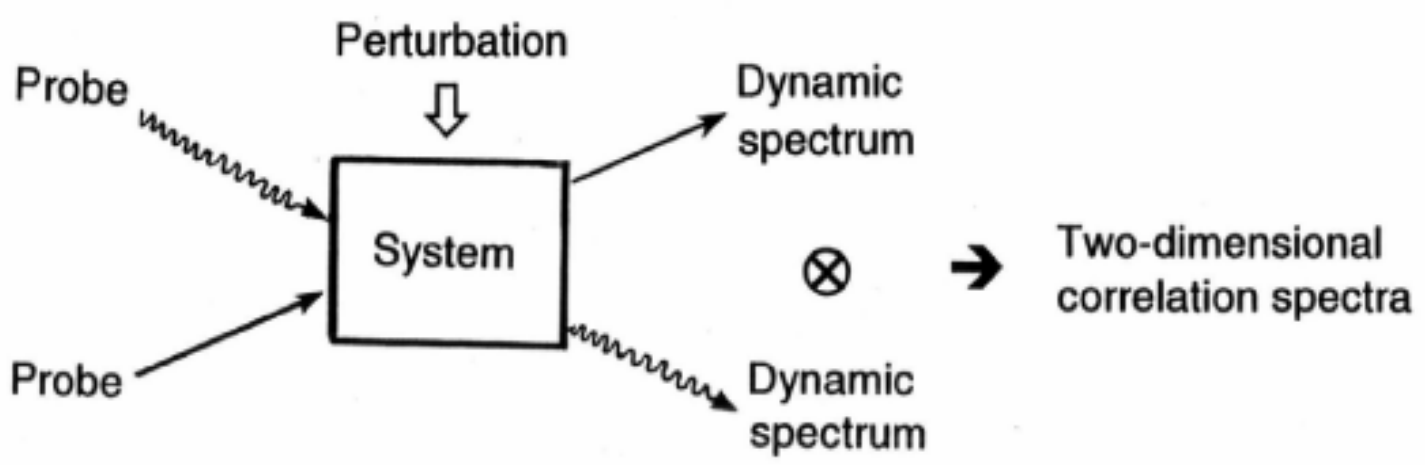
- Highly ordered crystals (I) grow **first** when *Nodax*^{TM} is cooled from the melt
- Less ordered (II) crystals grow **later,** while the amorphous component keeps decreasing as the temperature is further lowered

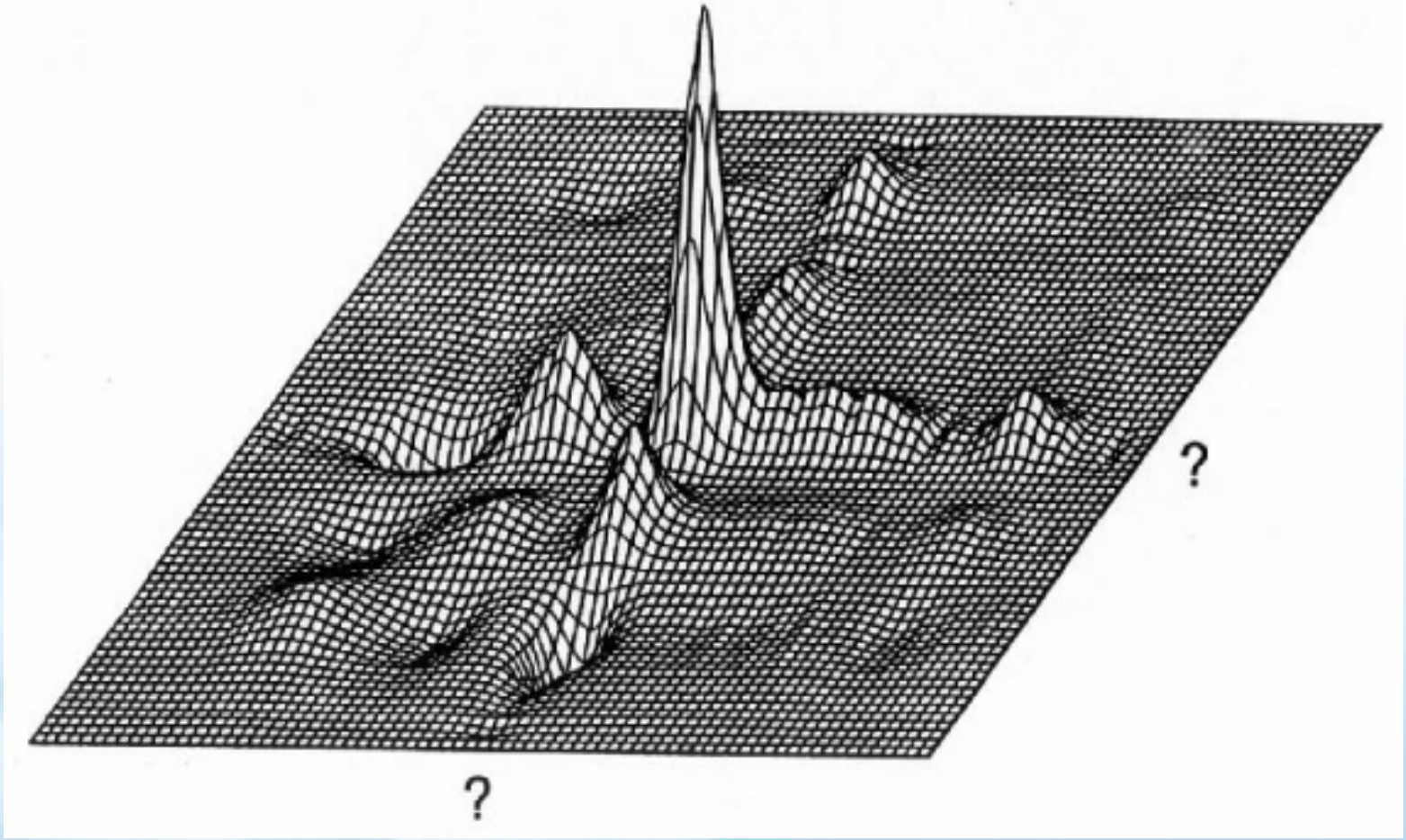
Two-Dimensional Correlation Spectroscopy

<IR, IR>
<Raman, Raman>
(SAXS, SAXS>
<UV, UV>
<NIR, NIR>
etc.

or

<IR, Raman>
<SAXS, IR>
<ESR, Acoustic>
<Microwave, SANS>
<UV, NMR>
etc.



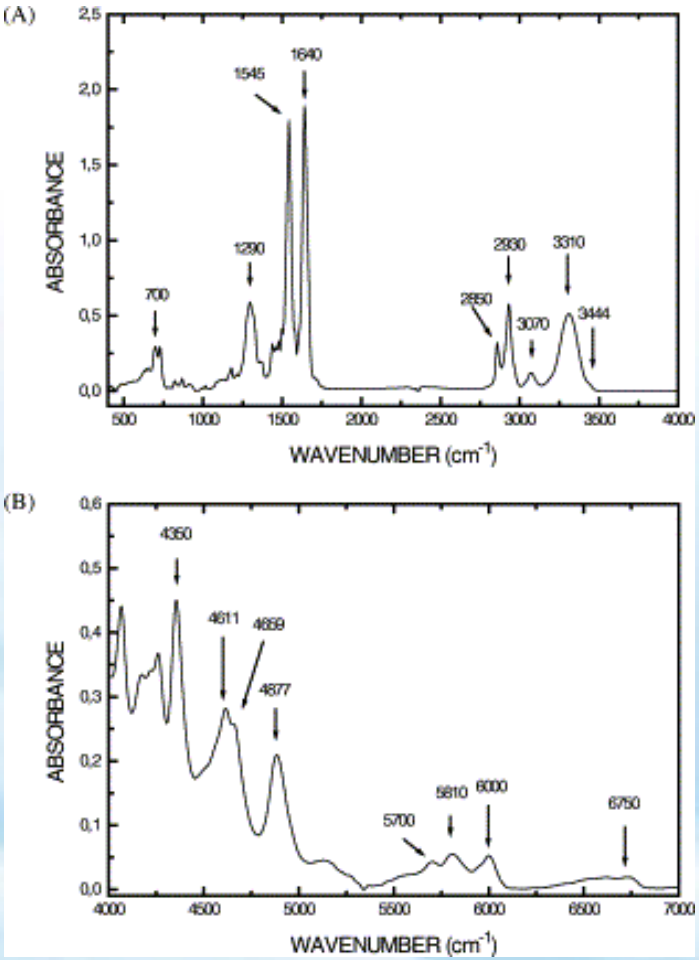


无定形聚酰胺的二维近红外相关光谱研究

摘要

利用二维近红外相关光谱研究了25–200 ℃的无定形聚酰胺。检测到5种不同的CH结构，其中两种对温度相应较灵敏，检测到自由的和氢键结合的NH，其中自由的NH又分为两种。

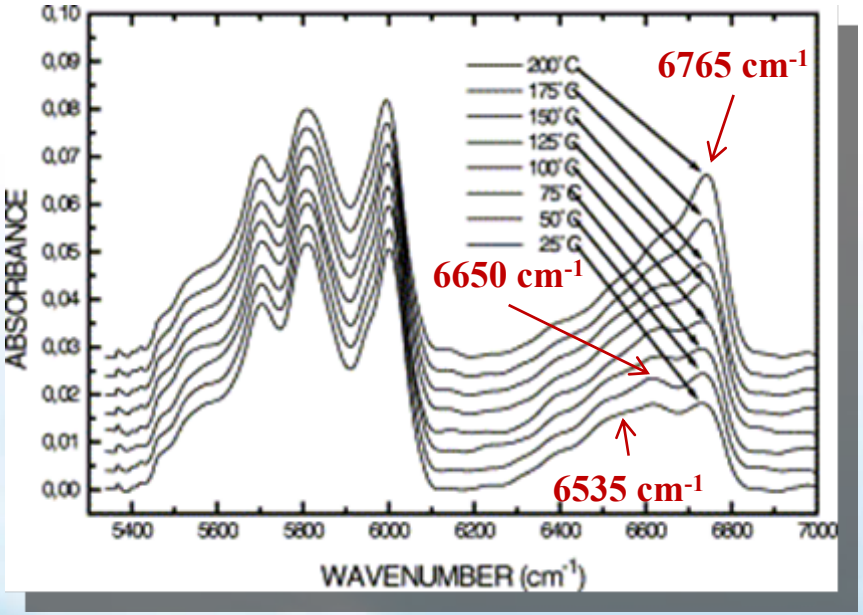
中红外近红外吸收峰归属表



Wavenumber (cm^{-1})	Intensity	Tentative assignment
3444	w	$\nu(NH)_f$
3310	s	$\nu(NH)_b$
3080	w	$\nu_{ar}(CH)$/2* Amide II
2930	s	$\nu_{as}(CH_2)$
2850	s	$\nu_{as}(CH_2)$
1640	s	Amide I
1545	s	Amide II
1290	m	Amide III
700	m	Amide V
6765	w	$2*\nu(NH)_f$
6520	m	$2*\nu(NH)_b$
6010	m	$2*\nu_{ar}(CH)$
5980	m	$2*\nu_{ar}(CH)$
5900	m	$2*\nu_{ar}(CH)$
5810	m	$2*\nu_{as}(CH_2)$
5690	m	$2*\nu_s(CH_2)$
4877	m	$\nu(NH)_b$+Amide II
4659	m	3*Amide II
4611	m	$\nu(NH)_b$+Amide III
4350	s	$\nu_s(CH_2)+\nu_{as}(CH_2)$

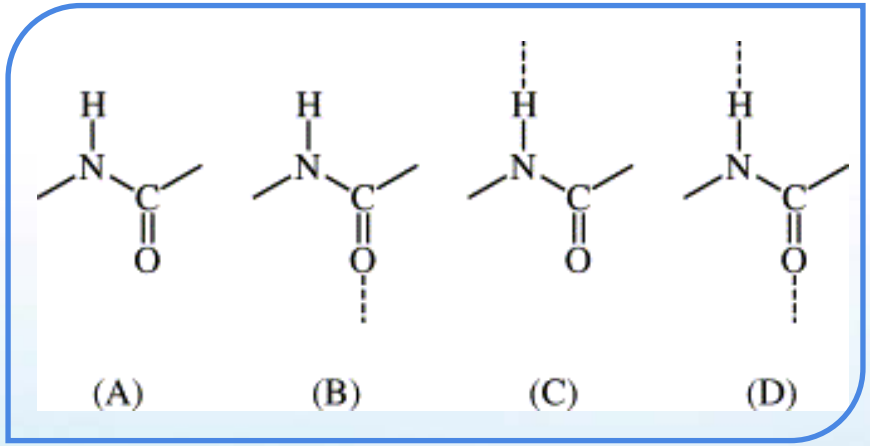
近红外变温实验结果

聚酰胺中不同氢键结构



Temperature-dependent FTNIR spectra obtained from 25 to 200 ℃ of the investigated amorphous polyamide in the spectral range 5400–7000 cm^{-1}.

Bruker IFS 88, 256scan, 4 cm^{-1}, 5℃ step

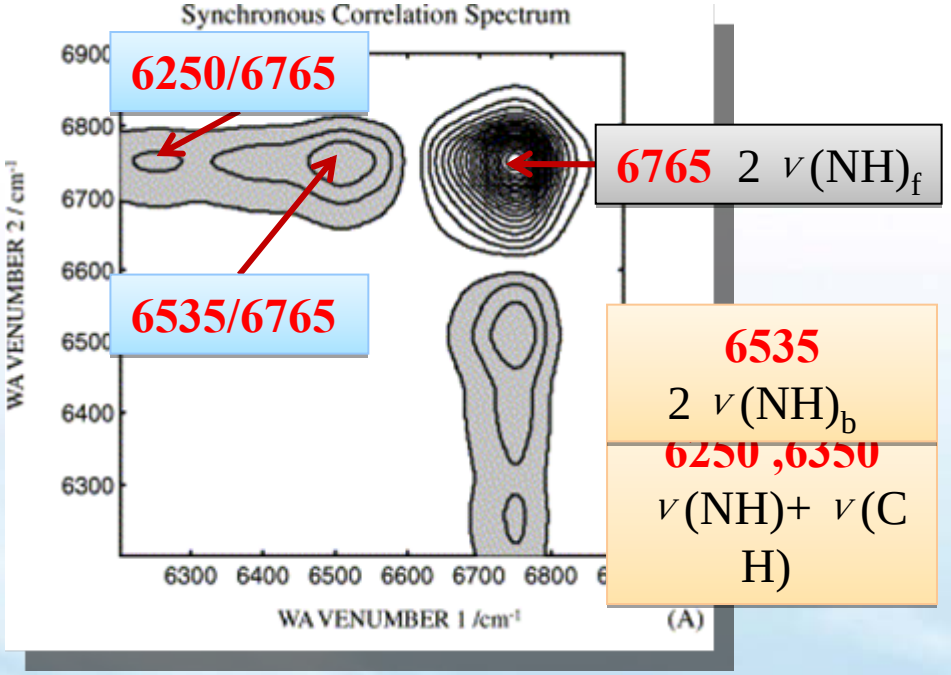


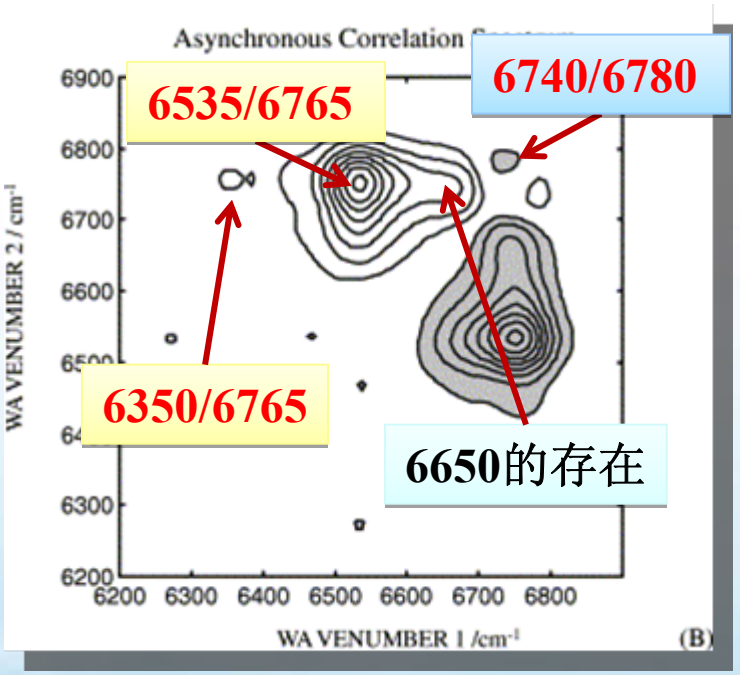
特征峰随温度上升的变化规律

波数(cm^{-1})	峰位置	峰强度
6765	不变	快速增加
6650	不变	小幅增加
6535	蓝移	减弱

二维相关谱图
(6200–6900 cm^{-1})

正峰　负峰　自相关





同步谱图负交叉峰说明吸收峰变化的方向相反，正峰则表示相同

6765 可能来源于6740与6780两个峰

结论

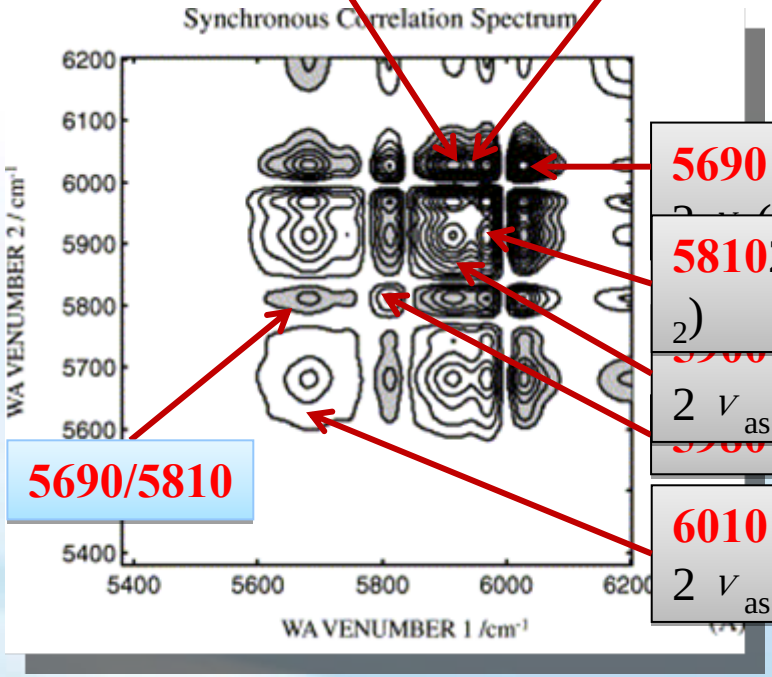
6535 变化先于6765

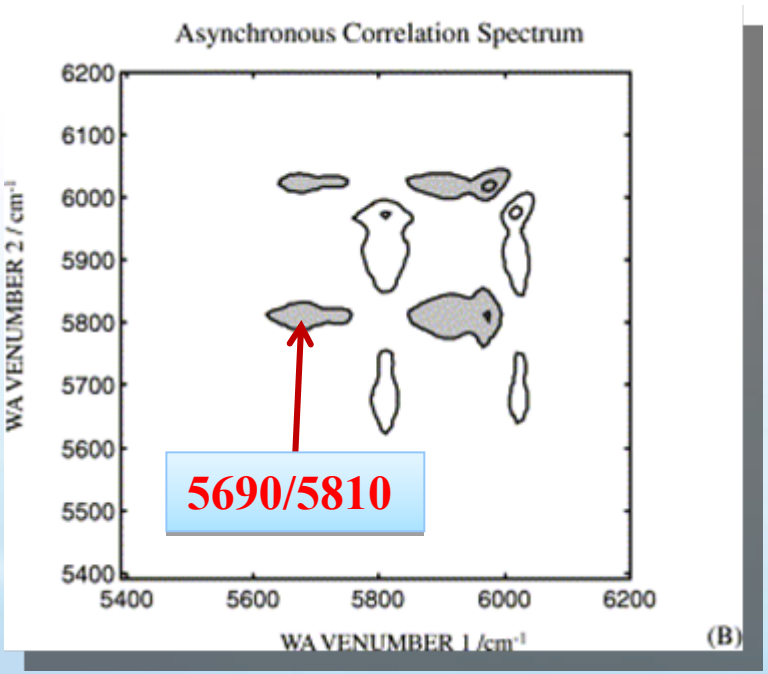
6780 变化先于6740

6350 变化先于6765

二维相关谱图 (5400–6200 cm^{-1})

正峰　负峰　自相关





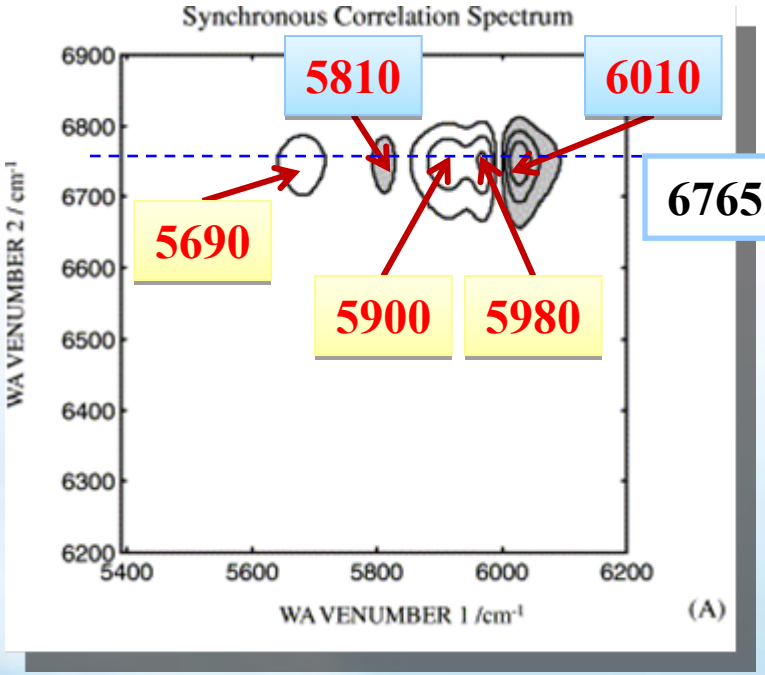
同步谱图存在五个自相关峰

结论

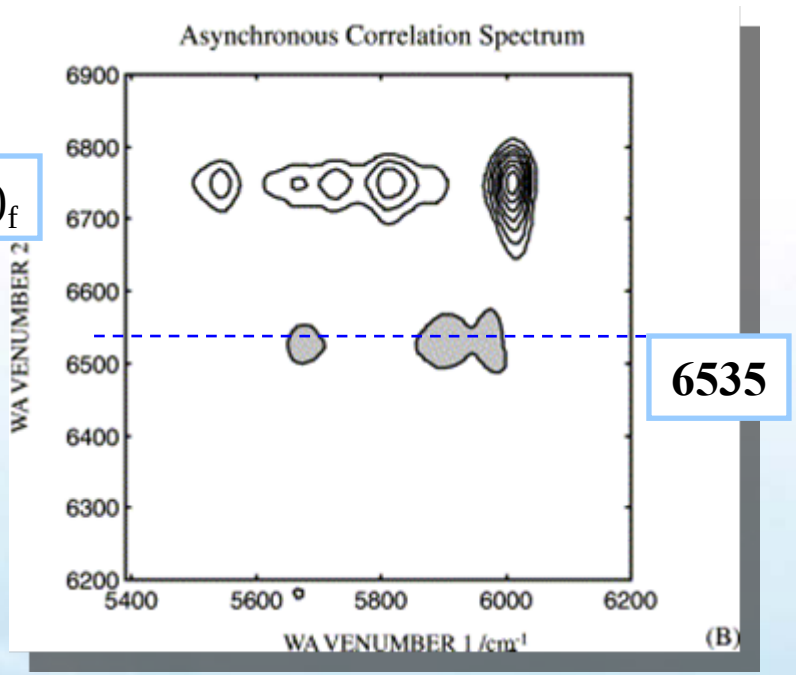
5810 变化先于5690

6010 变化先于5900, 5980

二维相关谱图(5400–6200 vs 6200–6900 cm^{-1})



6765 2 ν(NH)$_f$



CH与NH振动区域的关联

结论

5690, 5990, 5980变化先于6765

6535变化先于5690, 5990, 5980

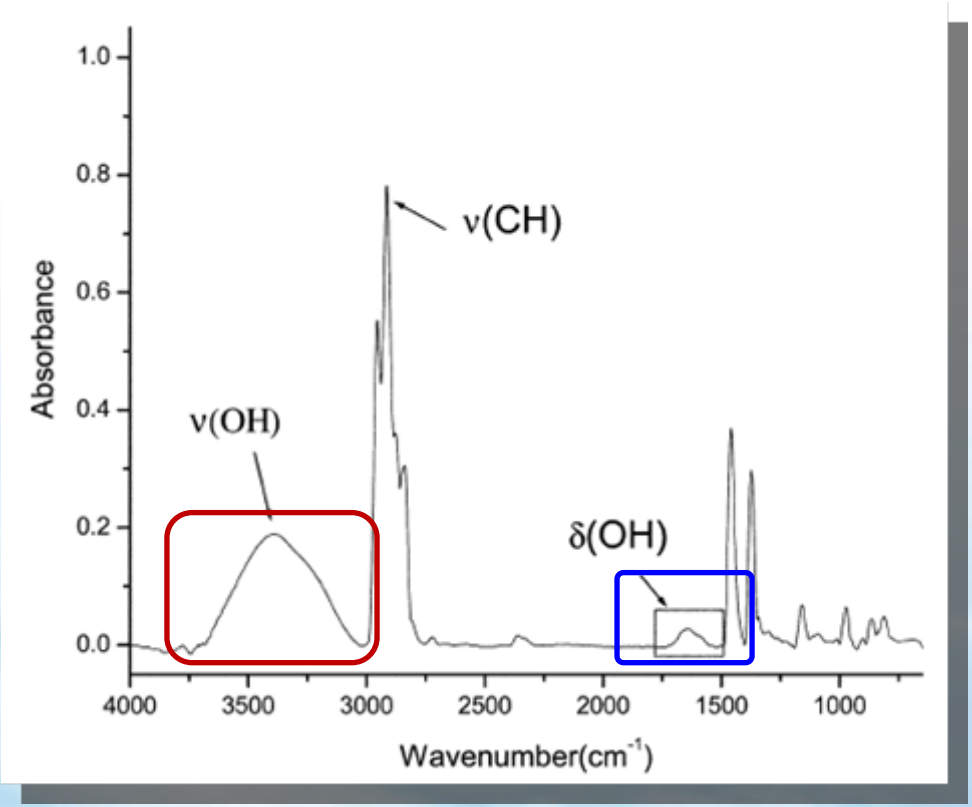
5810与6010对温度变化敏感

聚丙烯膜中水扩散的二维ATR-FTIR光谱研究

摘要

利用二维ATR-FTIR光谱研究水在聚丙烯膜中的扩散动力学。通过研究1800-1500 cm^{-1}区域，分析得到三种不同结构水分子：强氢键结合水(1676)，中强氢键结合水(1645)及自由水(1592)

课题研究背景



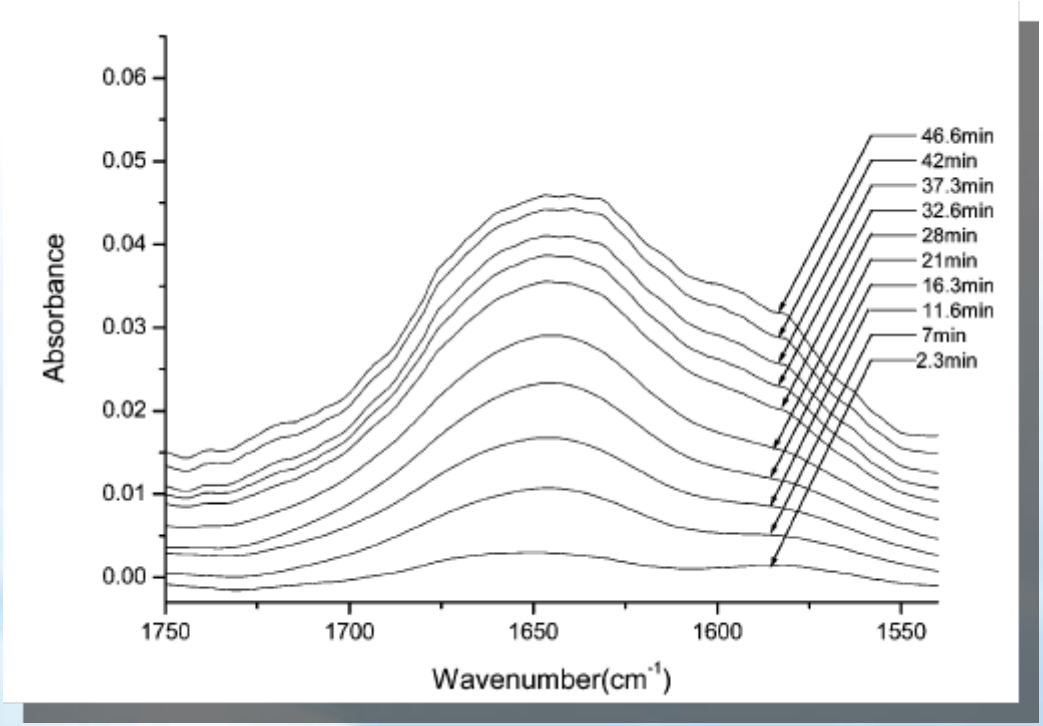
ATR-FTIR spectrum of sorbed water in S-PP in the range 4000-650 cm $^{-1}$.

水的伸缩振动区域(3000-4000 cm^{-1})重叠峰较多，分析困难

水的弯曲振动区域(1500-1700 cm^{-1})重叠峰较少，强度偏低

通过二维相关分析手段提高谱图分辨率分析水的弯曲振动区域

变温实验条件及数据



ATR-FTIR spectra of O-H bending band in the range 1750-1540 cm^{-1}.

制样方法

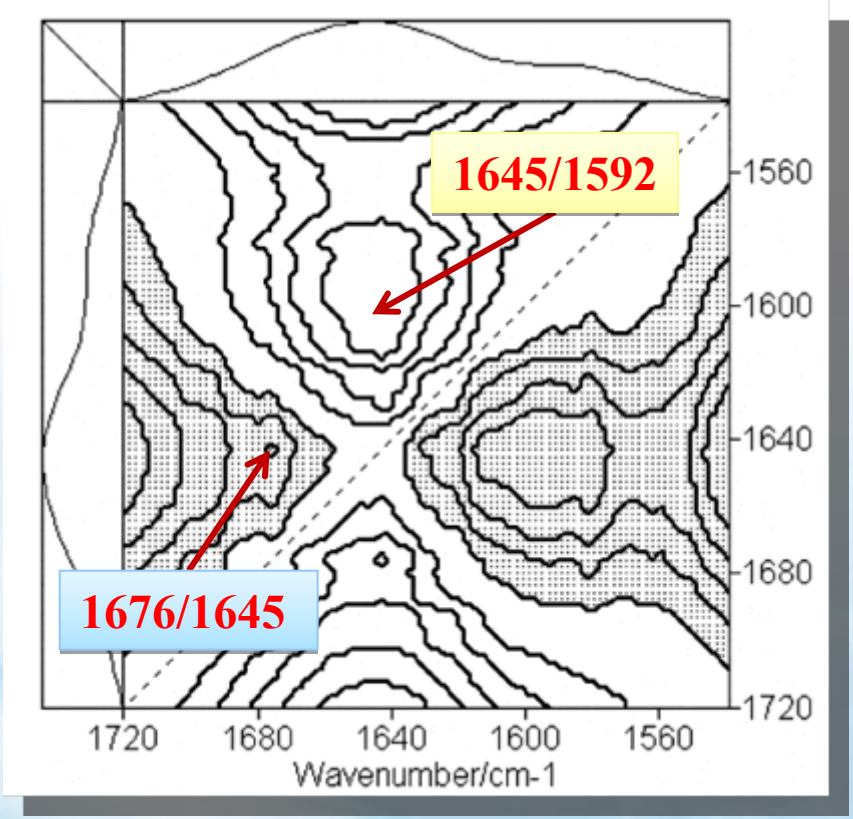
将聚丙烯溶于二甲苯后浇膜，在室温下于真空烘箱中存放24 h

仪器及实验

Nexus470及ATR压板附件，16scan，4cm^{-1}

将吸水滤纸附于膜表面，每2.5min采集数据

二维相关谱图 (1500–1800 cm^{-1})



Asynchronous 2D correlation spectra of water bending band in the range 1720-1540 cm^{-1}.

不同结构水	峰位置
Type I water	1676
强氢键结合水	
Type II water	1645
中强氢键结合水	
Type III water	1592
极弱氢键结合水（自由水）	

正峰　负峰

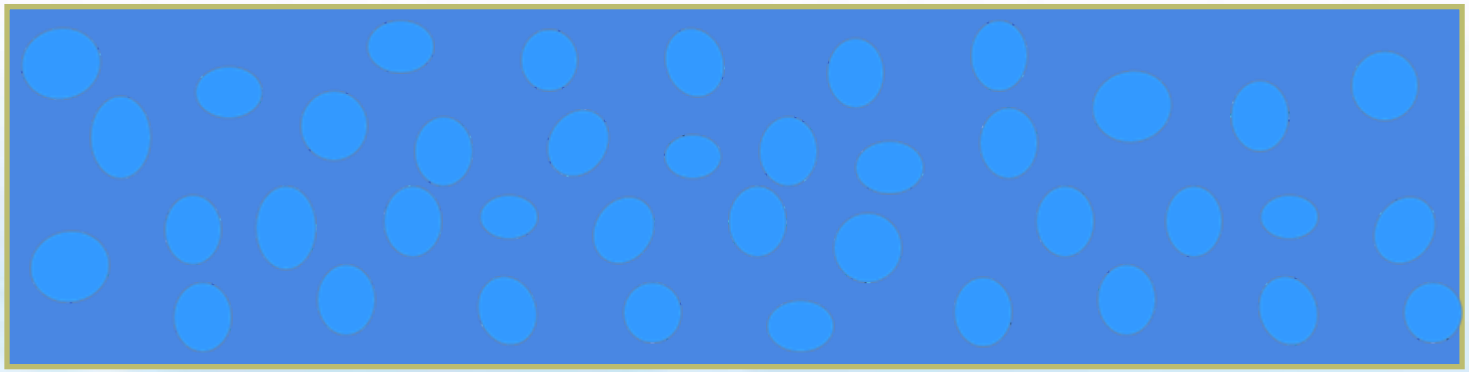
先后顺序：1645→1676→1592

相关机理解释

顺序

Type II　　Type III　　Type I

聚丙烯膜



一般纯水中以Type II型水分子居多， Type III型水分子体积较大，因此移动速度比Type II型水分子慢，PP膜中孔道被水填满后，Type I型水分子结构出现

尼龙6中脱水过程的二维近红外相关光谱研究

摘要

利用二维近红外相关光谱研究了不同温度下（50和80 ℃ ）时尼龙6的脱水行为。实验表面在不同温度下，尼龙6存在不同脱水机理。

实验条件及仪器设备

样品制备及处理条件

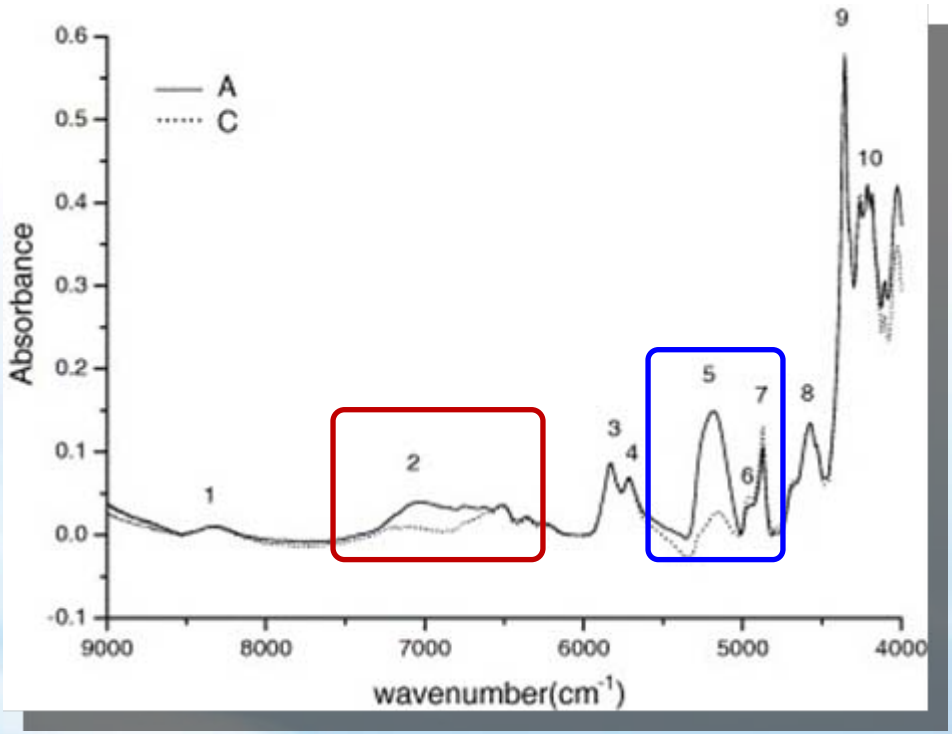
Sample	Preparation	Treatment
A	Immersed in a water bath over 12 h	Heated at 80 °C for about 1.5 h
B	Immersed in a water bath over 16 h	Heated at 50 °C for about 2 h
C	Kept in a desiccator	Heated at 80 °C for about 1.5 h
D	Kept in a desiccator	Heated at 50 °C for about 2.5 h

仪器及实验条件

Nexus 470 FT-IR/NIR，液氮冷却MCT检测器，分辨率4cm^{-1}

分别在50和80 ℃恒温扫描100min, 扫描范围3000-11000cm^{-1}

尼龙6近红外光谱归属

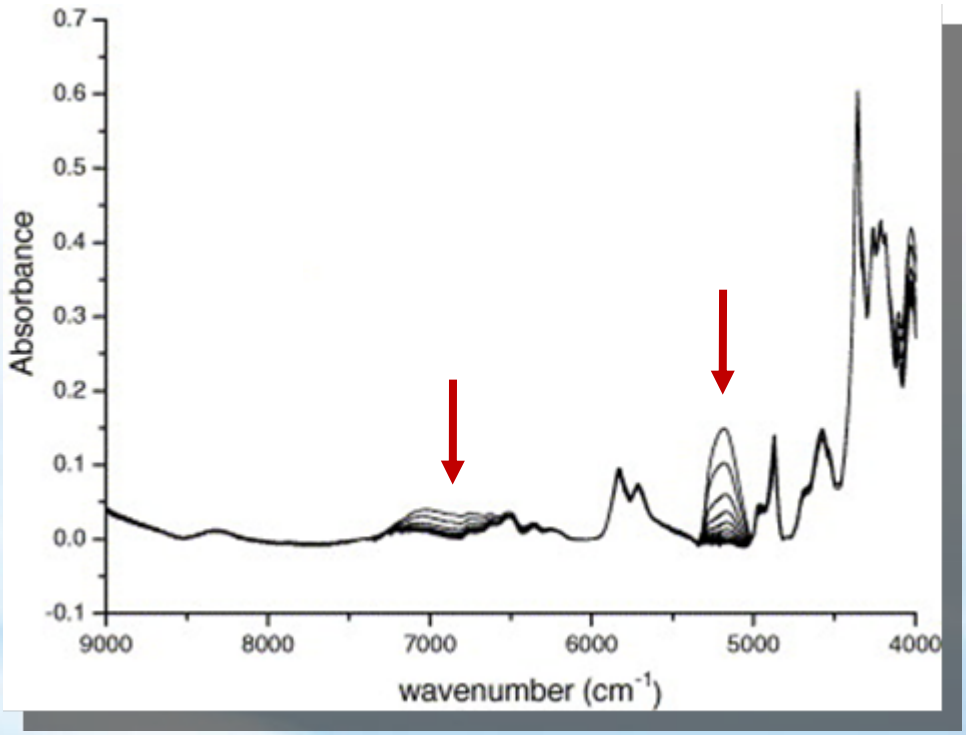


Near-infrared spectra recorded from the original films of sample A (–) and sample C (…) at room temperature.

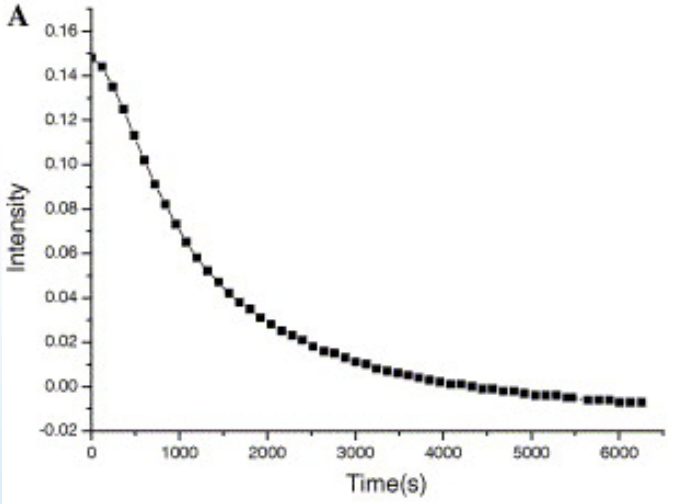
尼龙6近红外光谱归属表

1	8310	$3^*\nu(CH_2)$
	7220	$2^*\nu_{as}(CH_2) + \delta(CH_2)$
2	7020	$\nu_1(OH) + \nu_3(OH)$
	6750	$\nu_1(OH) + \nu_3(OH)$ and $2^*\nu(NH)_f$
	6500	$2^*\nu(NH)_b$
3	5860	$2^*\nu_{as}(CH_2)$
4	5740	$2^*\nu_s(CH_2)$
5	5280	$\nu_2(OH) + \nu_3(OH)$ (s_0)
	5230	$\nu_2(OH) + \nu_3(OH)$ (s_1)
	5140	$\nu_2(OH) + \nu_3(OH)$ (s_2)
6	4990	$\nu(NH)_b$ + amide I
7	4880	$\nu(NH)_b$ + amide II
	4718	Amide I + 2*amide II
8	4628	$\nu(NH)_b$ + amide III
9	4374	$\nu_s(CH_2) + \delta(CH_2)$
10	4283	$\nu_s(CH_2) + \delta(CH_2)$
	4230	$\nu_s(CH_2) + \gamma_w(CH_2)$
	4193	$\nu_s(CH_2) + \gamma(CH_2)$

80℃时尼龙膜脱水谱图



Near-infrared spectra of sample A in the range 9000 – 4000 cm^{-1} recorded every 10 min during isothermal treatment at 80 ° C.

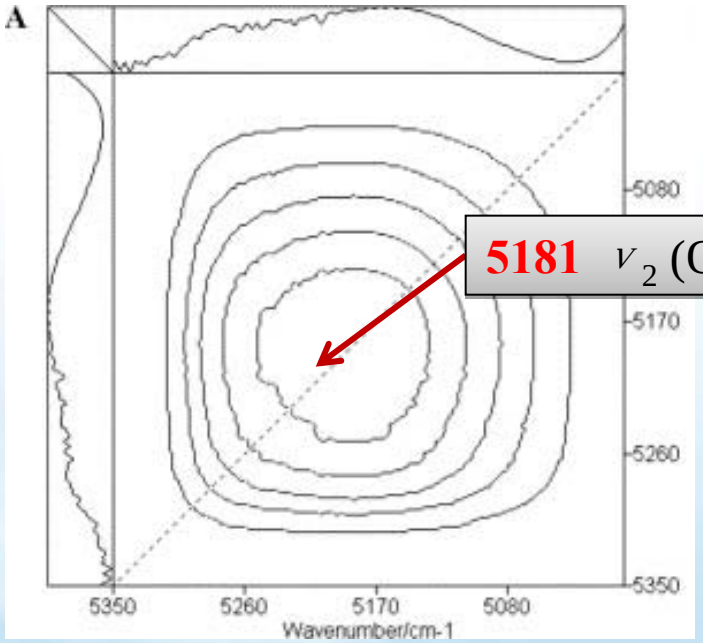


5200cm^{-1}峰强随时间变化图

脱水过程呈现非线性变化

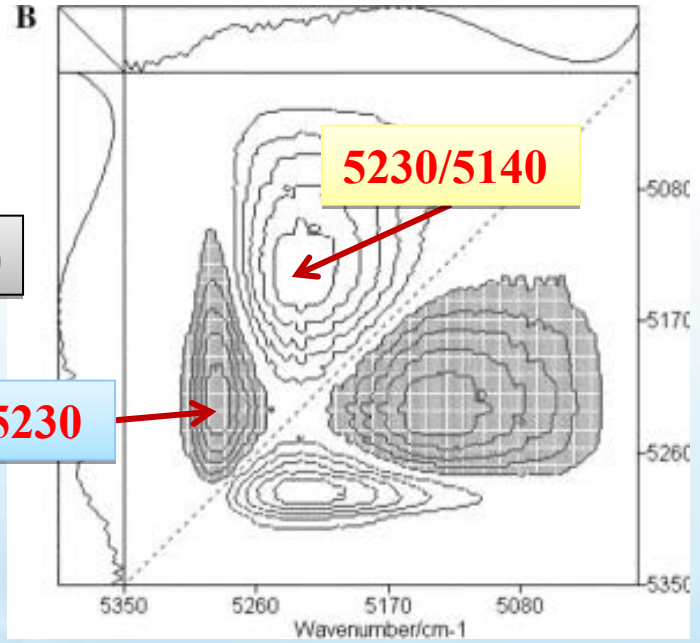
样品A二维相关谱图 (5000–5350 cm^{-1})

正峰　负峰　自相关



80 ℃

5181　ν_2 (OH)+ ν_3(OH)



5181 cm^{-1} 峰可能有三个来源

5280：自由水分子(s_0)

5230：一端氢键水分子(s_1)

5140：两端氢键水分子(s_2)

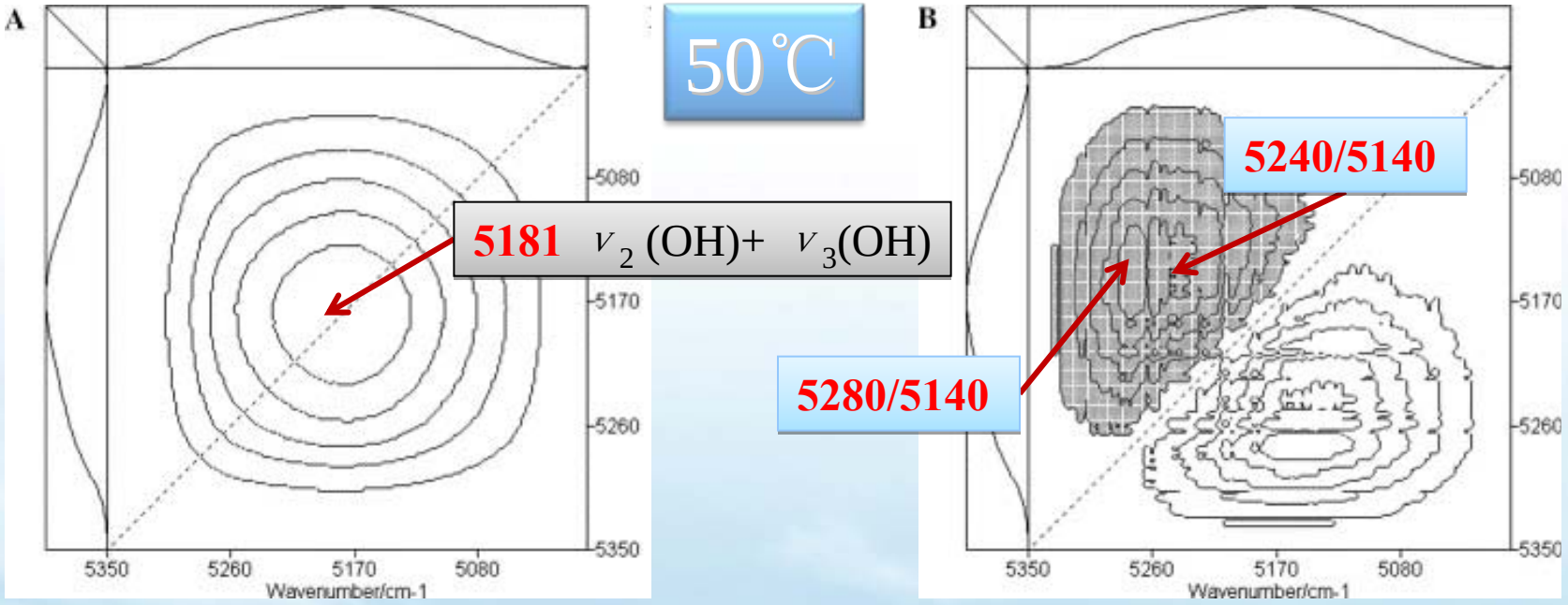
结论

5230 变化先于5280

5230 变化先于5140

样品B二维相关谱图 (5000–5350 cm^{-1})

正峰　负峰　自相关



两端氢键水分子(s_2)　变化先于　自由水分子(s_0)　一端氢键水分子(s_1)

结论　5140 变化先于5280　5140 变化先于5240

实验结果机理解释

5280：自由水分子(s_0)　　**5230**：一端氢键水分子(s_1)　　**5140**：两端氢键水分子(s_2)

50℃

温度较低，能量较小

$s_2 \rightarrow s_1$

$s_1 + s_2 \rightarrow s_0$

80℃

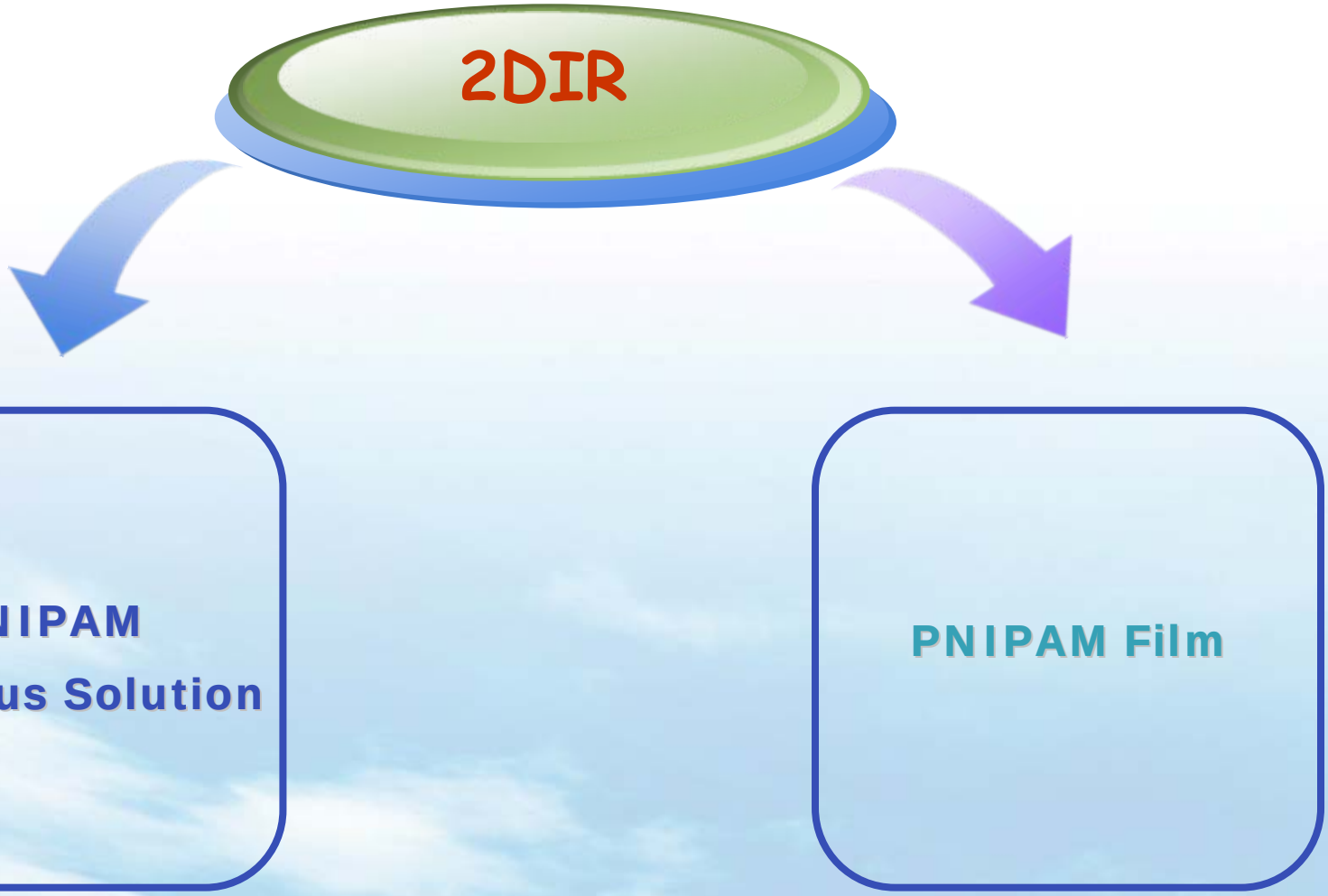
温度较高，能量较大

$s_2 \rightarrow s_0$

$s_1 \rightarrow s_0$

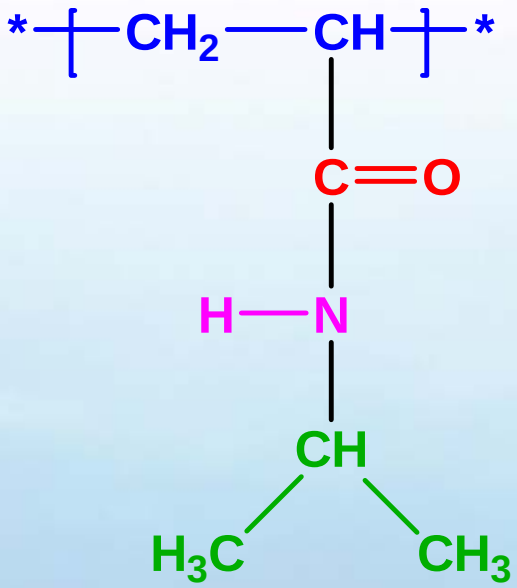
FTIR and 2D-IR Spectroscopic Study on Poly N-isopropylacrylamide (PNIPAM)

2008-12-7

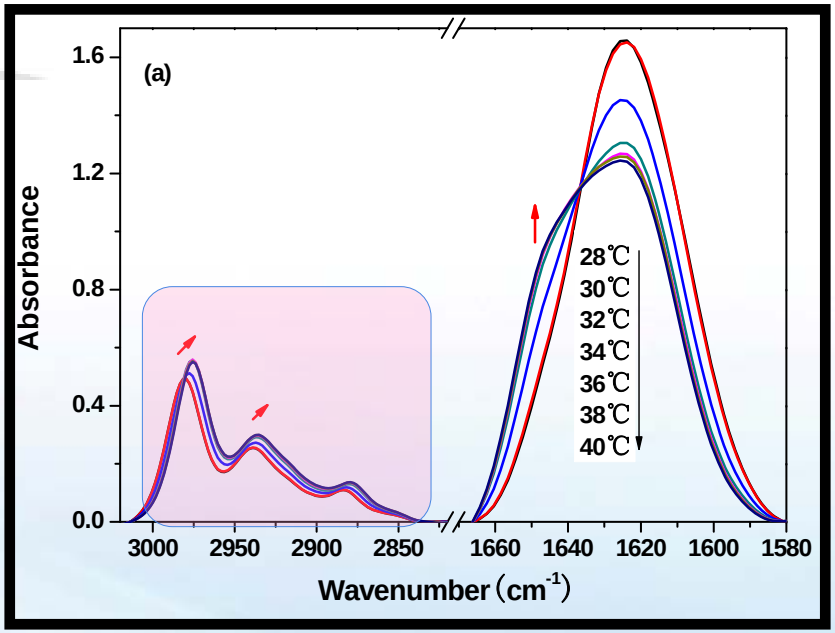

2DIR
PNIPAM
Aqueous Solution
PNIPAM Film

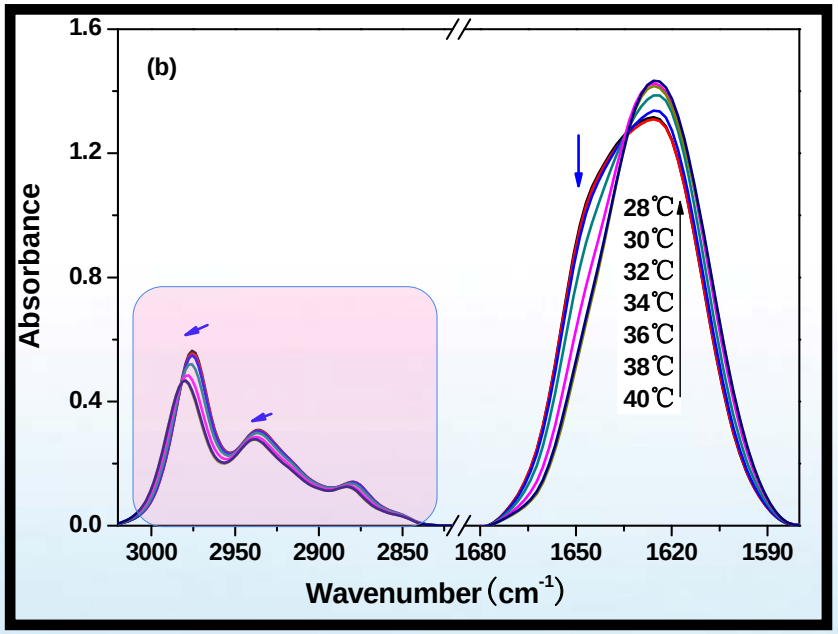
Poly N-isopropylacrylamide (PNIPAM)

Chemical Structure



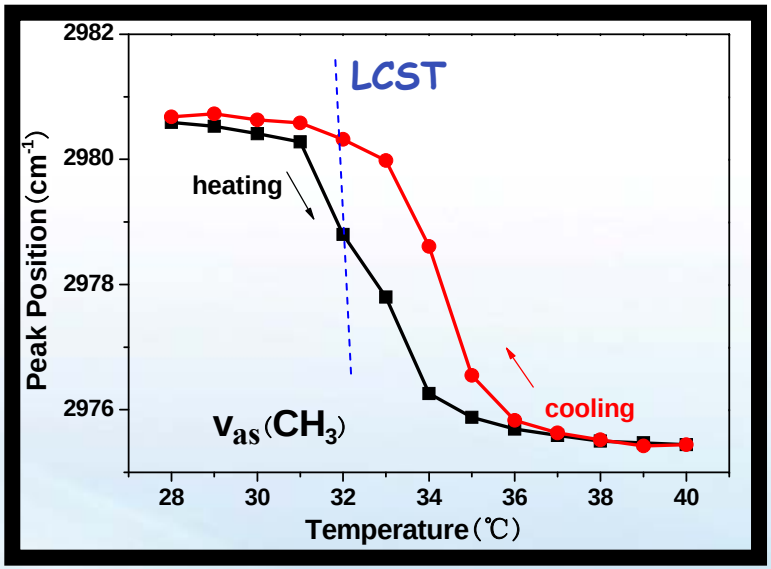
LCST～32℃

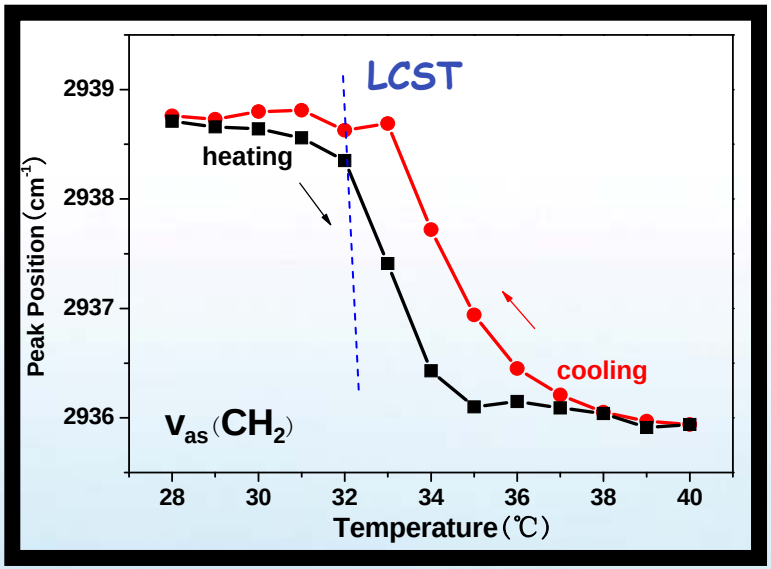




FTIR spectra of PNIPAM 20wt% D_2O solution (28 ≒ 40 ℃)

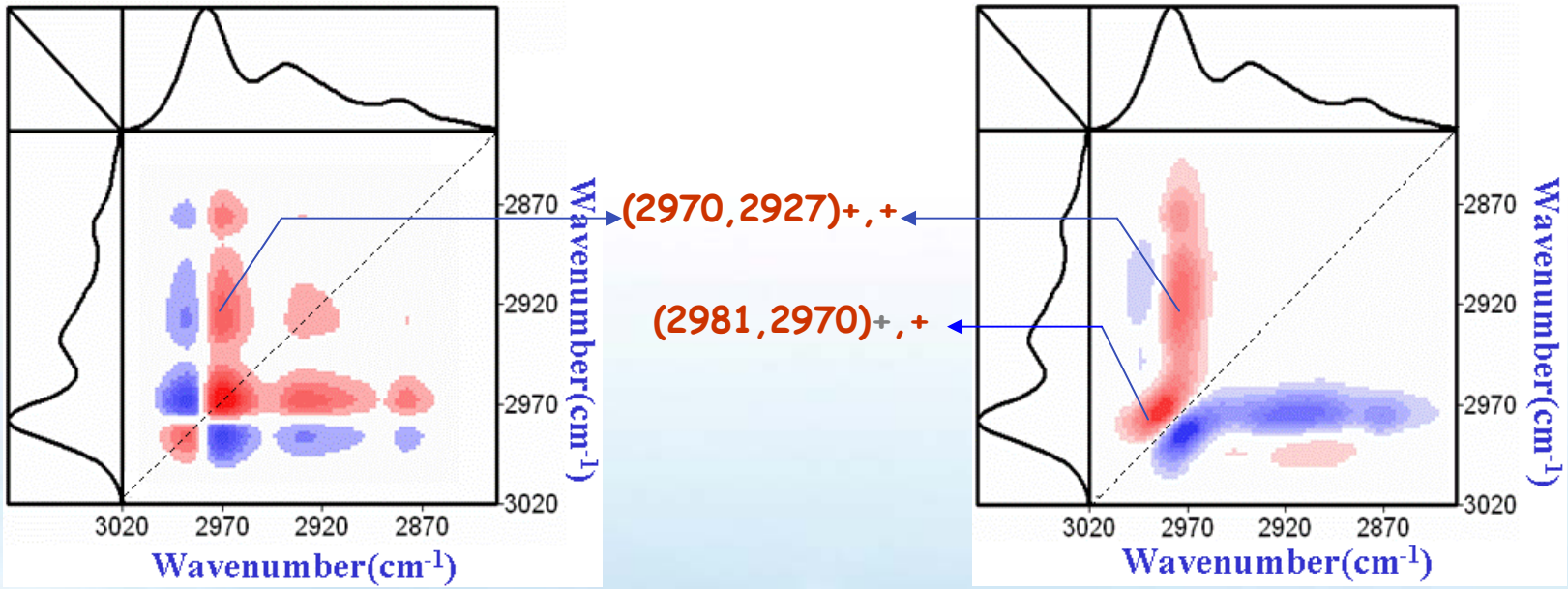
Quantitative Analysis





1 Reversible dehydration/hydration process of C-H group

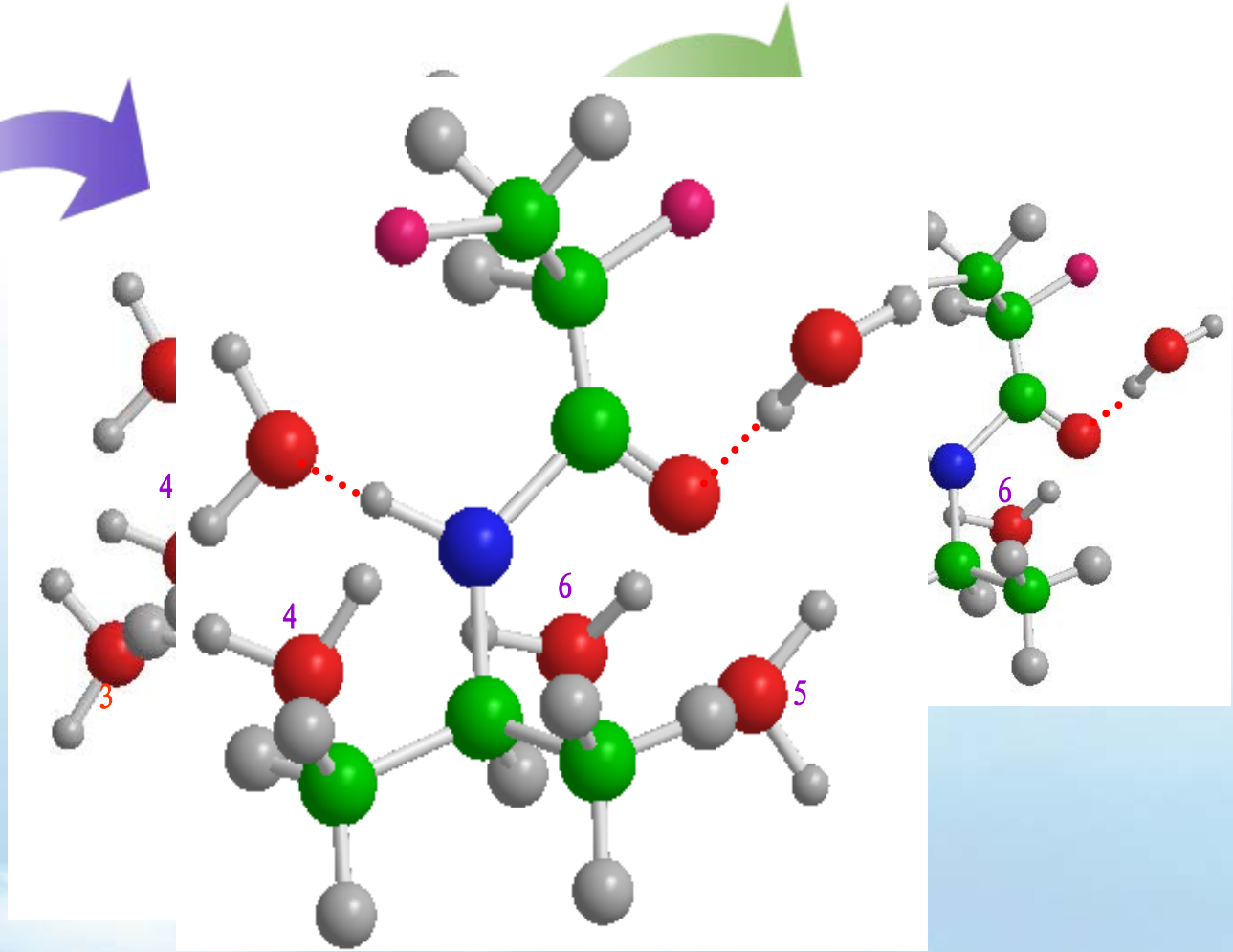
Investigation of CH Bands - 2DIR



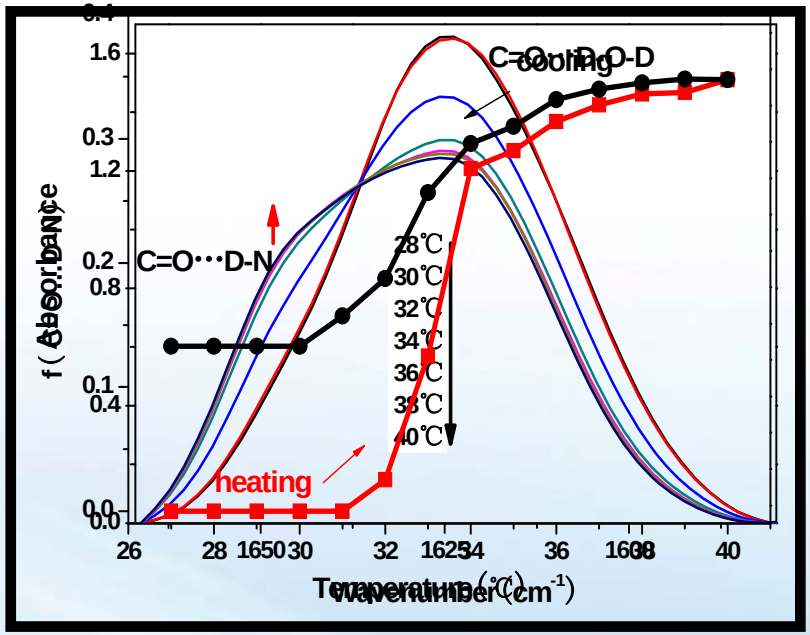
2 Two-step dehydration/hydration process of CH_3

3 Dehydration of side-chain > main-chain aggregation

Two-step dehydration mechanism of CH_3



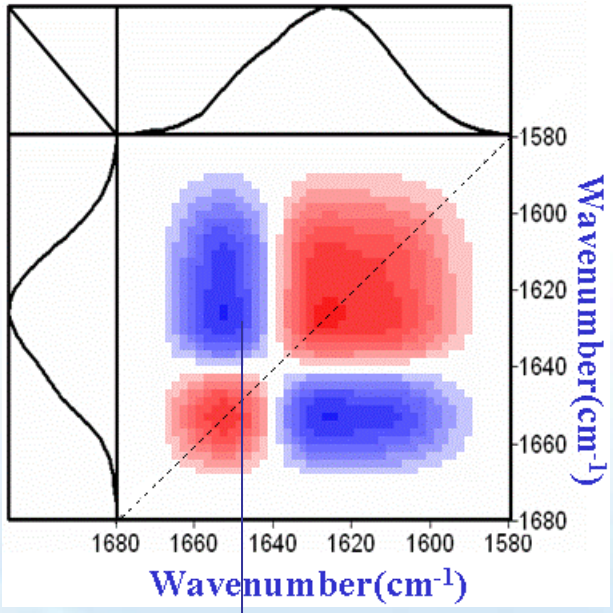
Investigation of Amide I band-FTIR

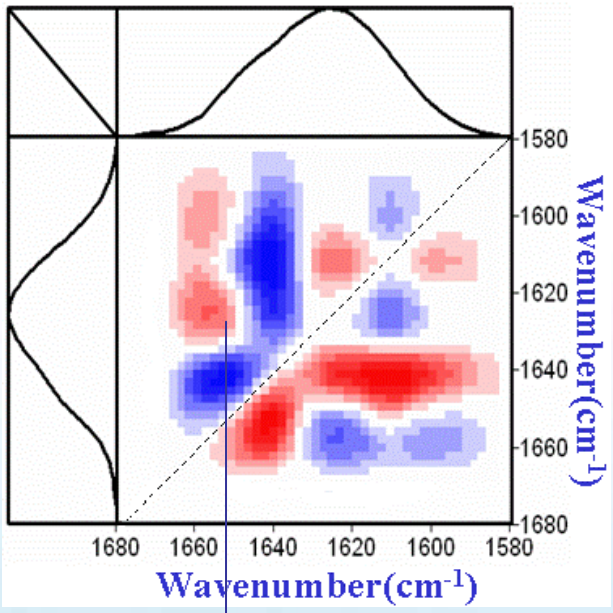


Wavenumber(cm^{-1})	Assignment
1649	ν (C=O···D-N)
1624	ν (C=O···D-O-D)

$$f(C{=}O\cdots D\text{-}N) = A1649/[A1649 + A1625*(\varepsilon\ 1649/\ \varepsilon\ 1625)]$$

Investigation of Amide I band -2DIR



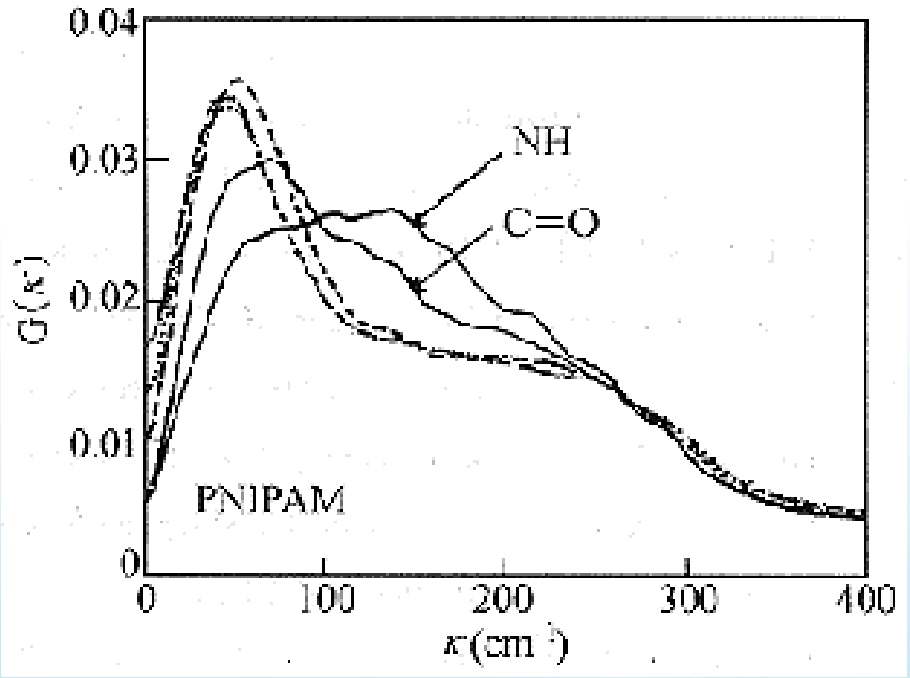


(1649,1624)-,+

1624 > 1649

C=O···D-O-D > C=O···D-N

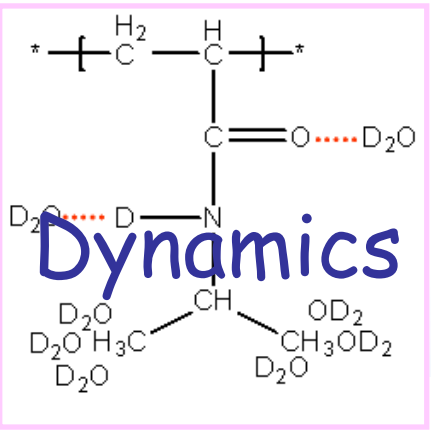
Dehydration and Hydration of N-D : Spectral Density Method



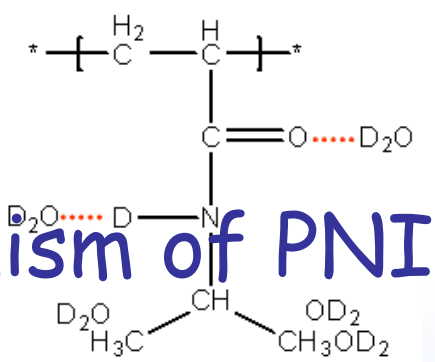
The formation and destruction of N-H···O-H > C=O···H-O-H

Macromolecule, 1996, 29, 6761

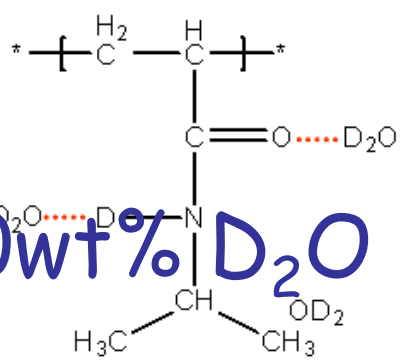
Dynamics mechanism of PNIPAM 20wt% D_2O solution during heating



Dehydration of CH_3(I)

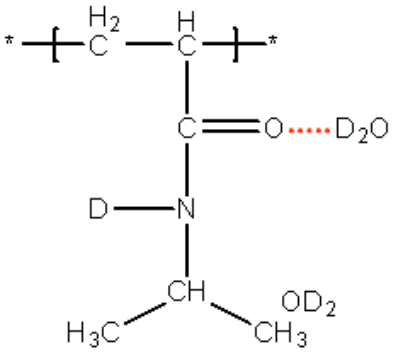


Dehydration of CH_3(II)

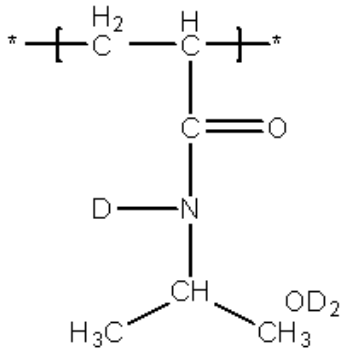


Diffusion and aggregation of the main chains

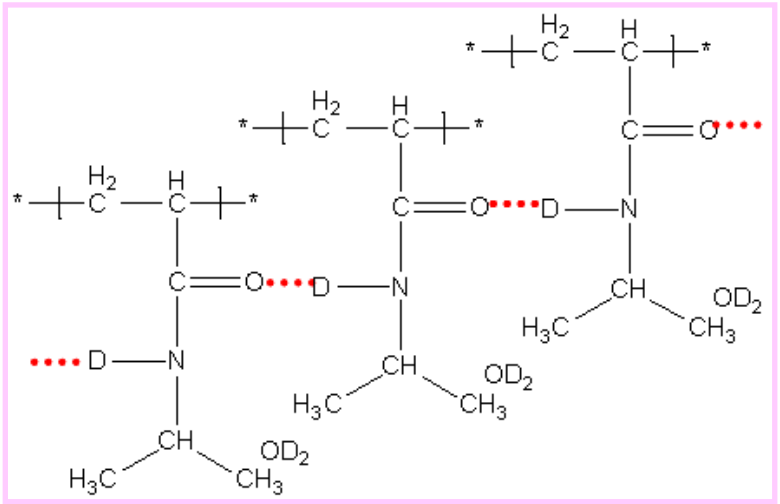
Breakage of N-D···O-D



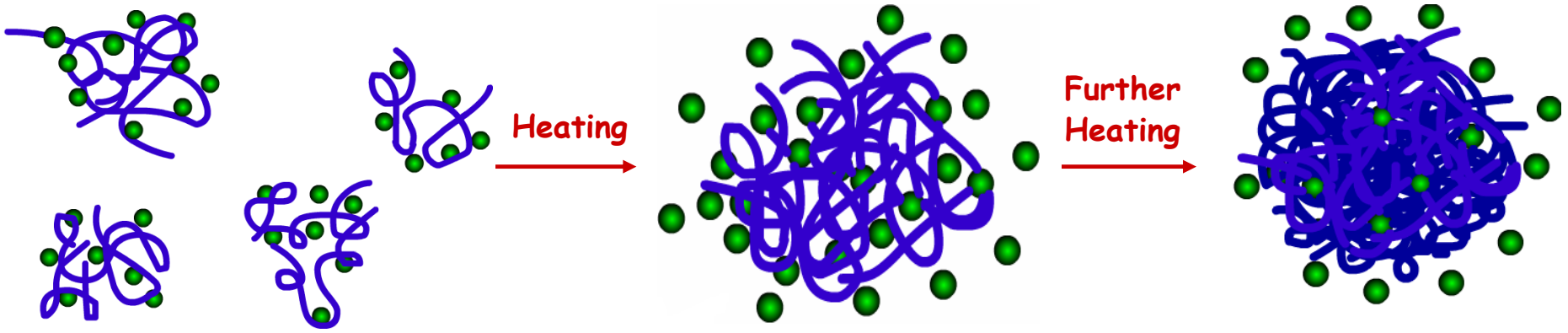
Breakage of C=O···D-O



Formation of C=O...D-N



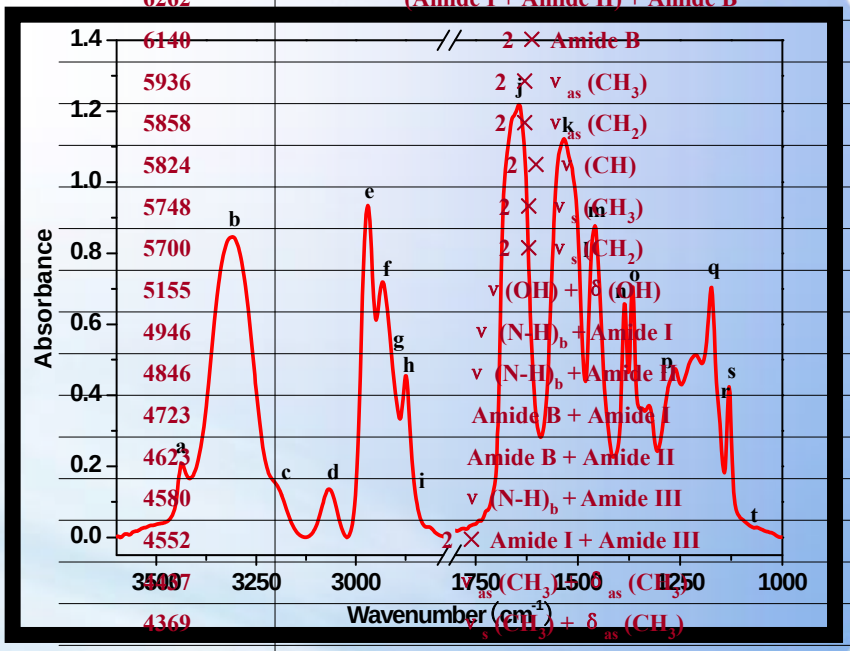
Dynamics of chains in PNIPAM aqueous solution during heating



20wt%

Assignments of overtone and combination bands in the NIR spectrum of PNIPAM

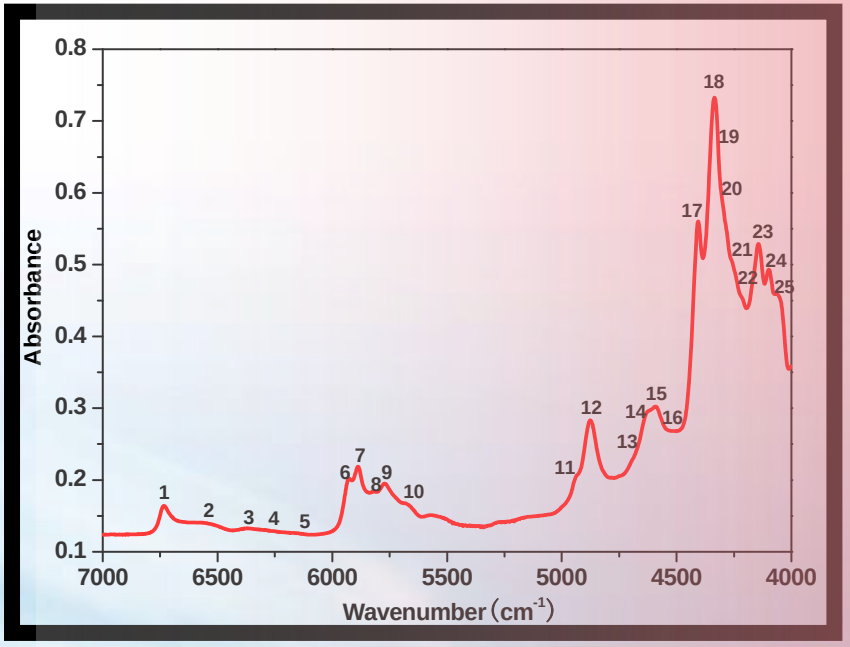
6874	2 × ν (N-H)$_f$
6600	2 × ν (N-H)$_b$
6370	Amide B + ν (N-H)$_b$
6262	(Amide I + Amide II) + Amide B
6140	// 2 × Amide B
5936	2 × ν$_{as}$ (CH$_3$)
5858	2 × ν$_{as}$ (CH$_2$)
5824	2 × ν (CH)
5748	2 × ν$_s$ (CH$_3$)
5700	2 × ν$_s$ (CH$_2$)
5155	ν (OH) + δ (NH)
4946	ν (N-H)$_b$ + Amide I
4846	ν (N-H)$_b$ + Amide II
4723	Amide B + Amide I
4623	Amide B + Amide II
4580	ν (N-H)$_b$ + Amide III
4552	2 × Amide I + Amide III
4507	ν$_{as}$ (CH$_3$) + ν$_{as}$ (CH$_3$)
4369	ν$_s$ (CH$_3$) + δ$_{as}$ (CH$_3$)
4352	ν$_{as}$ (CH$_3$) + δ$_s$ (CH$_3$)
4308	ν$_{as}$ (CH$_2$) + δ$_{as}$ (CH$_2$)
4286	ν$_s$ (CH$_3$) + δ$_s$ (CH$_3$)
4218	ν$_s$ (CH$_2$) + δ$_s$ (CH$_2$)
4141	ν$_{as}$ (CH$_3$) + CH$_3$ skeletal
4098	ν$_{as}$ (CH$_3$) + CH$_3$ rocking
4064	ν$_{as}$ (CH$_3$) + CH$_2$ rocking



MIR Spectrum of PNIPAM film (RT)

	Wavenumber (cm^{-1})	Assignment
a	3437	ν (N-H)$_f$
b	3300	ν (N-H)$_b$
c	3190	Amide I + Amide II
d	3070	Amide B
e	2968	ν$_{as}$ (CH$_3$)
f	2929	ν$_{as}$ (CH$_2$)
g	2912	ν (CH)
h	2874	ν$_s$ (CH$_3$)
i	2850	ν$_s$ (CH$_2$)
j	1646	Amide I
k	1546	Amide II
l	1469	δ$_{as}$ (CH$_3$)
m	1458	δ$_{as}$ (CH$_2$)
n	1387	δ$_s$ (CH$_3$)
o	1368	δ$_s$ (CH$_2$)
p	1280	Amide III
	1260	
q	1173	CH$_3$ skeletal
r	1155	CH$_2$ skeletal
s	1132	CH$_3$ rocking
t	1096	CH$_2$ rocking

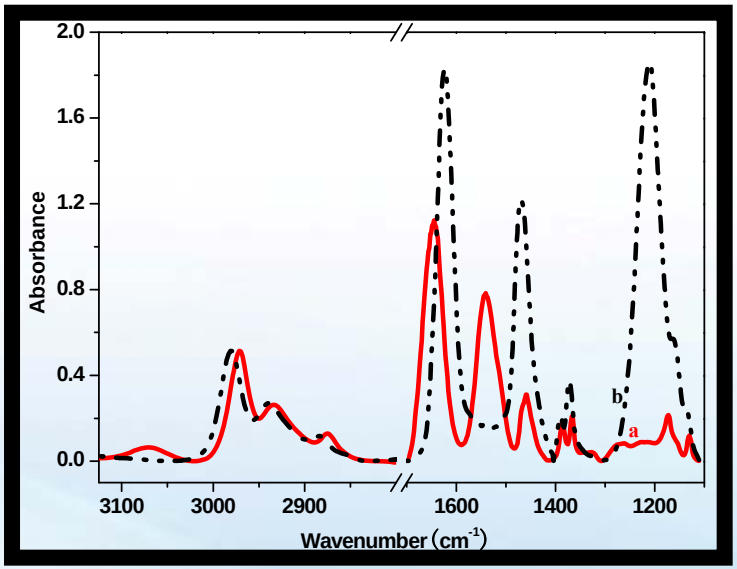
Assignments of overtone and combination bands in the NIR spectrum of PNIPAM



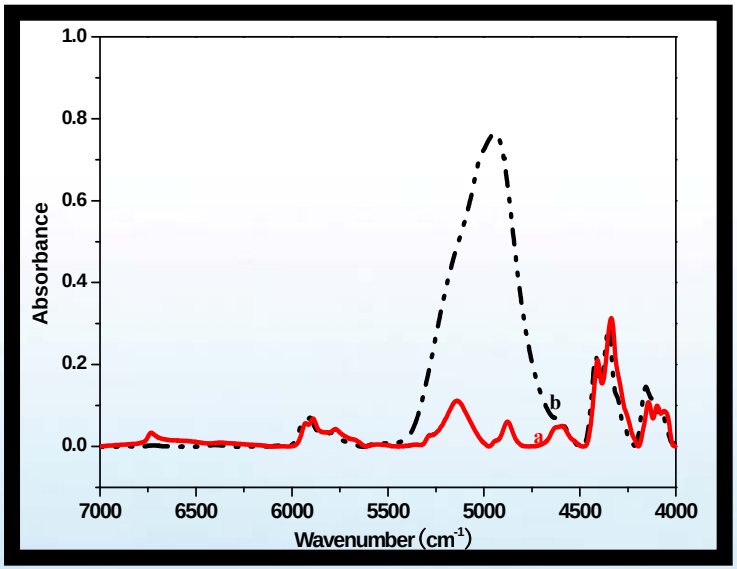
NIR Spectrum of PNIPAM film (RT)

	Wavenumber (cm^{-1})	Assignment
1	6736	$2 \times \nu\ (N\text{-}H)_f$
2	6550	$2 \times \nu\ (N\text{-}H)_b$
3	6368	Amide B + $\nu\ (N\text{-}H)_b$
4	6258	(Amide I + Amide II) + Amide B
5	6140	2 × Amide B
6	5933	$2 \times \nu_{as}\ (CH_3)$
7	5889	$2 \times \nu_{as}\ (CH_2)$
8	5823	$2 \times \nu\ (CH)$
9	5773	$2 \times \nu_{s}\ (CH_3)$
10	5675	$2 \times \nu_{s}\ (CH_2)$
11	5135	$\nu\ (OH) + \delta\ (OH)$
12	4945	$\nu\ (N\text{-}H)_b$ + Amide I
13	4878	$\nu\ (N\text{-}H)_b$ + Amide II
14	4701	Amide B + Amide I
15	4623	Amide B + Amide II
16	4580	$\nu\ (N\text{-}H)_b$ + Amide III
17	4529	2 × Amide I + Amide III
18	4408	$\nu_{as}\ (CH_3) + \delta_{as}\ (CH_3)$
19	4335	$\nu_{s}\ (CH_3) + \delta_{as}\ (CH_3)$
20	4329	$\nu_{as}\ (CH_3) + \delta_{s}\ (CH_3)$
21	4298	$\nu_{s}\ (CH_2) + \delta_{as}\ (CH_2)$
22	4243	$\nu_{s}\ (CH_3) + \delta_{s}\ (CH_3)$
23	4214	$\nu_{s}\ (CH_2) + \delta_{s}\ (CH_2)$
24	4138	$\nu_{as}\ (CH_3)$ + CH_3 skeletal
25	4098	$\nu_{as}\ (CH_3)$ + CH_3 rocking
26	4052	$\nu_{as}\ (CH_3)$ + CH_2 rocking

Deuteration studies-MIR&NIR



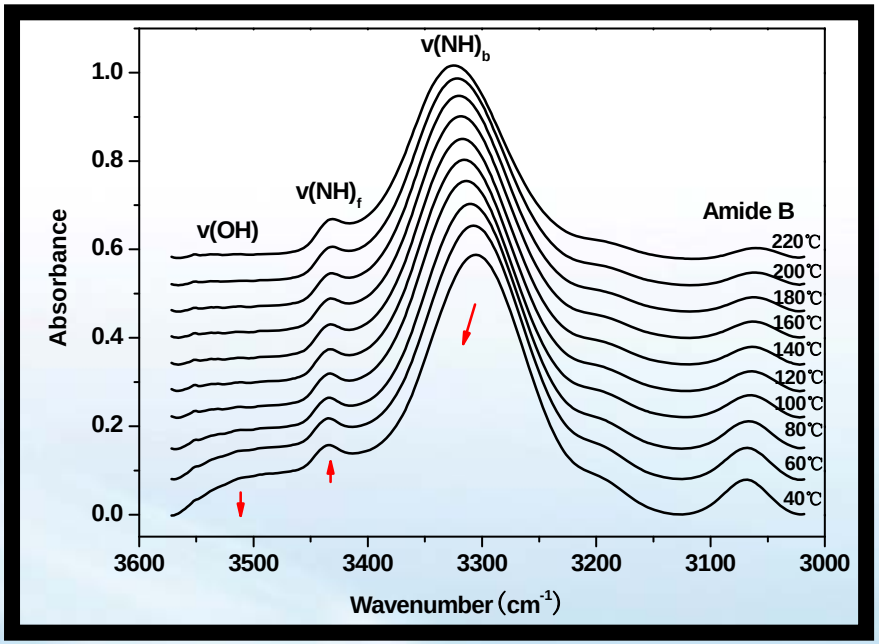
MIR Spectrum

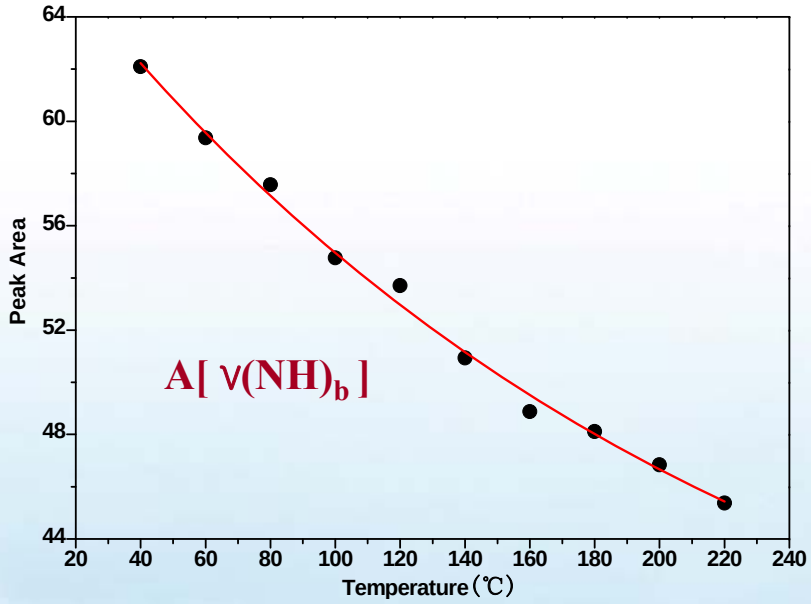


NIR Spectrum

Intensity Change: Peak of Amide groups

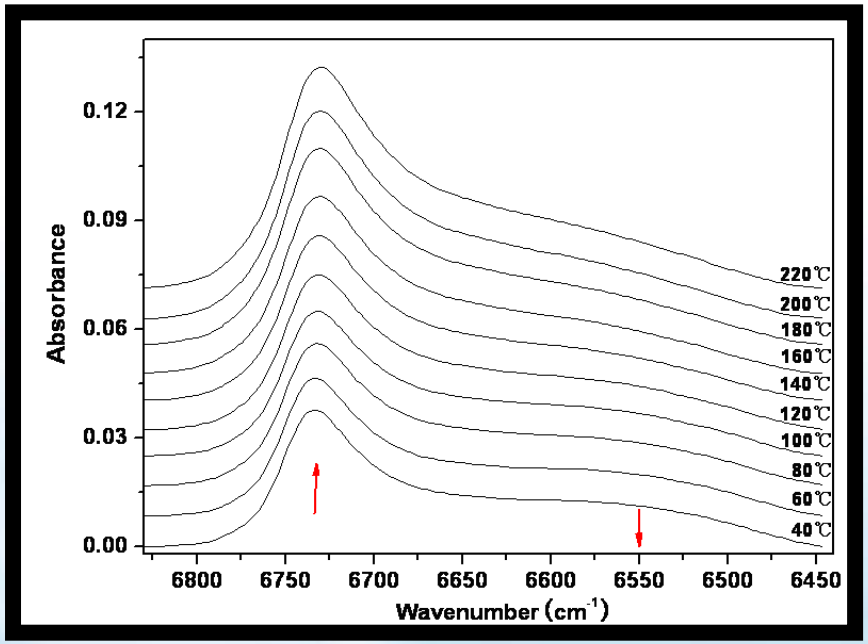
Variable Temperature Study -MIR

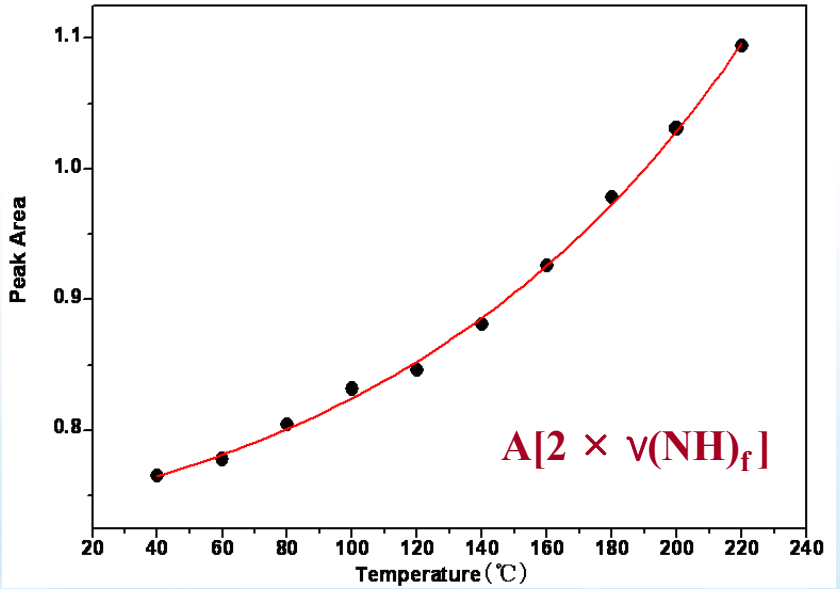




Change of NH bonding

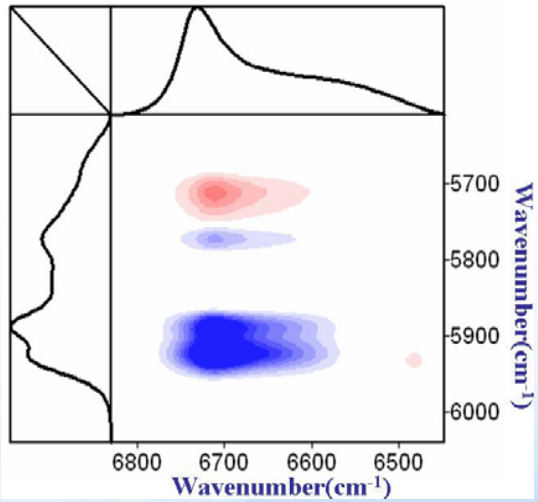
Variable Temperature Study -NIR

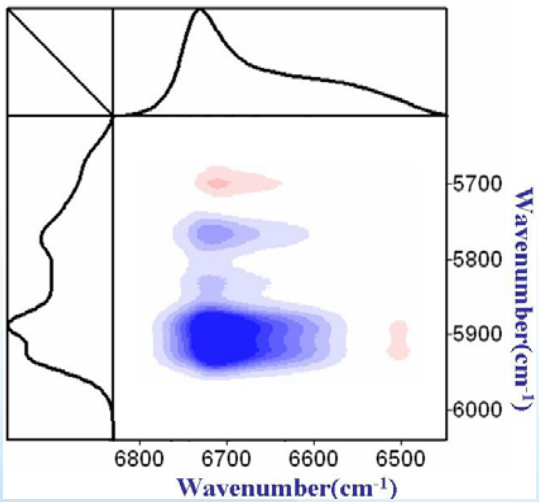




Change of free NH groups

2DIR-NH groups *vs.* CH groups





During heating, modifications of NH > conformational changes of hydrocarbon chains

$2\times \nu(NH)_b > 2\times (NH)_f > 2\times \nu_{as}(CH_3) > 2\times \nu_{as}(CH_2)$

2008年12月7日星期日

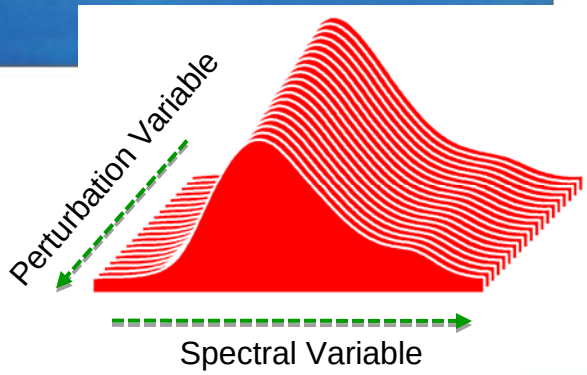
Application of Two-Dimensional Correlation Spectroscopy and Perturbation Correlation Moving Window

Supramolecular Self-Assembly Thermodynamic Mechanism of A Special Mesogen-Jacketed Liquid Crystalline Polymer

Generalized Two-Dimensional Correlation Spectroscopy

1. Reference spectrum (average spectrum):

$$\bar{y}(v) = \frac{1}{N}\sum_{j=1}^{N} y(v, p_j)$$

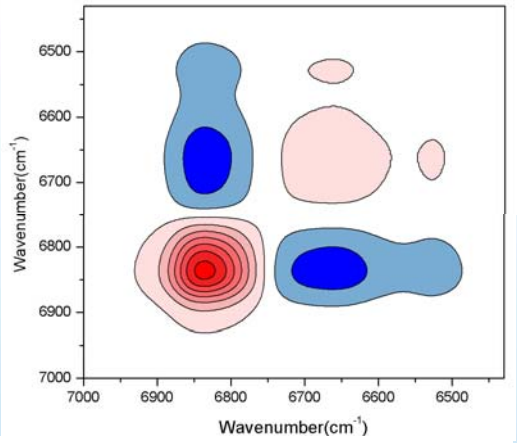


2. Dynamic spectrum:

$$\tilde{y}(v, p) = \begin{cases} y(v, p) - \bar{y}(v) & \text{for } 1 \le p \le N \\ 0 & \text{otherwise} \end{cases}$$

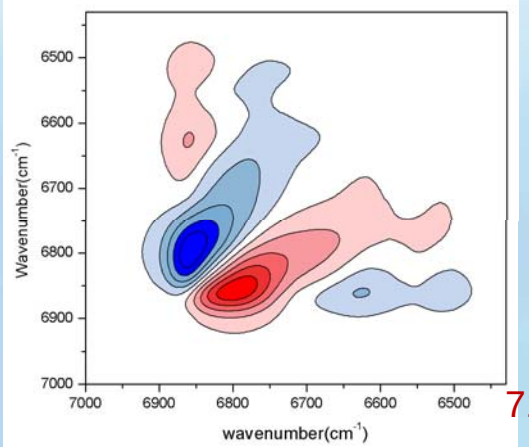
3. Synchronous 2D correlation spectrum:

$$\Phi(v_1, v_2) = \frac{1}{N-1}\sum_{j=1}^{N} \tilde{y}(v_1, p_j) \cdot \tilde{y}(v_2, p_j)$$



4. Asynchronous 2D correlation spectrum:

$$\Psi(v_1, v_2) = \frac{1}{N-1}\sum_{j=1}^{N} \tilde{y}(v_1, p_j) \cdot \sum_{k=1}^{N} M_{jk} \cdot \tilde{y}(v_2, p_k)$$



Hilbert-Noda transformation matrix

$$M_{jk} = \begin{cases} 0 & \text{if } j = k \\ \dfrac{1}{\pi(k-j)} & \text{otherwise} \end{cases}$$

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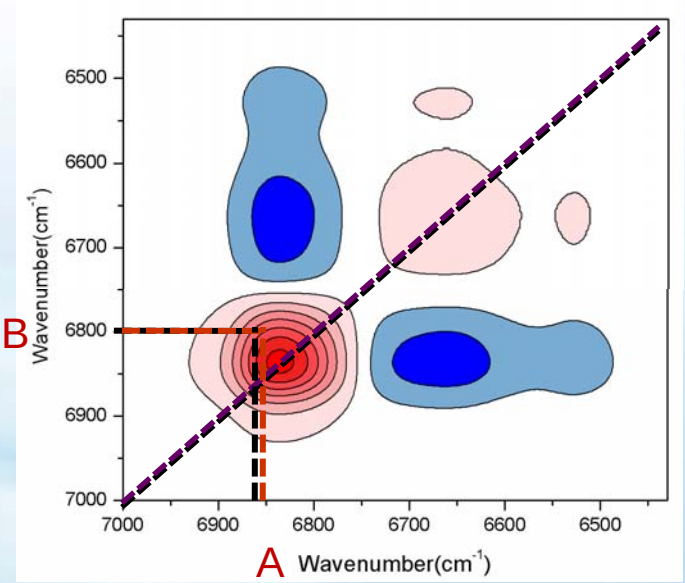
Generalized Two-Dimensional Correlation Spectroscopy

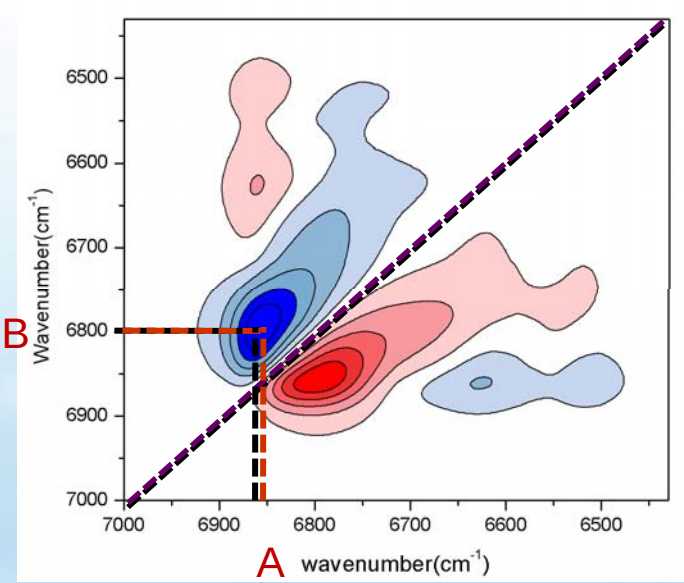
【Advantages of 2Dcos】

- Enhance the spectral resolution ;
- Discern the specific order taking place under perturbation. (Noda's Rule)

Synchronous Spectra (同步谱)



Asynchronous Spectra (异步谱)



Synchronous → positive

Asynchronous → negative

Conclusion: A and B both decrease (or increase);
B decreases prior to A

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Contents

- Generalized Two-Dimensional Correlation Spectroscopy
- Perturbation Correlation Moving Window
- Application

  PDBVT – poly[di(butyl) vinylterephthalate]

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Perturbation Correlation Moving Window

Moving Window 2D Correlation Spectroscopy (2000)

M. Thomas and H. Richardson, *Vib. Spectrosc*., 24, 137-146, (2000).

- search for the transition points

Perturbation Correlation Moving Window 2D Correlation Spectroscopy (2006)

Shigeaki Morita, et al*., Appl. Spectrosc.*, 60, 398-406, (2006).

- search for the transition points
- monitor complicated spectral variations along perturbation variable

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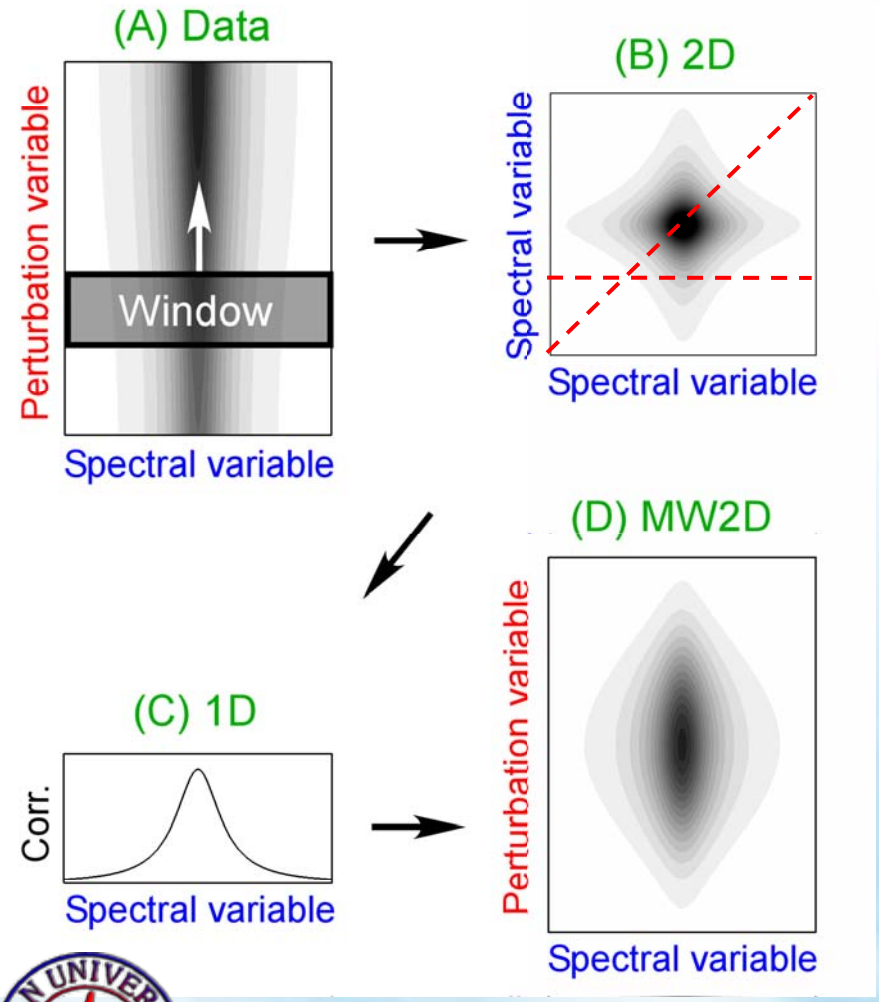
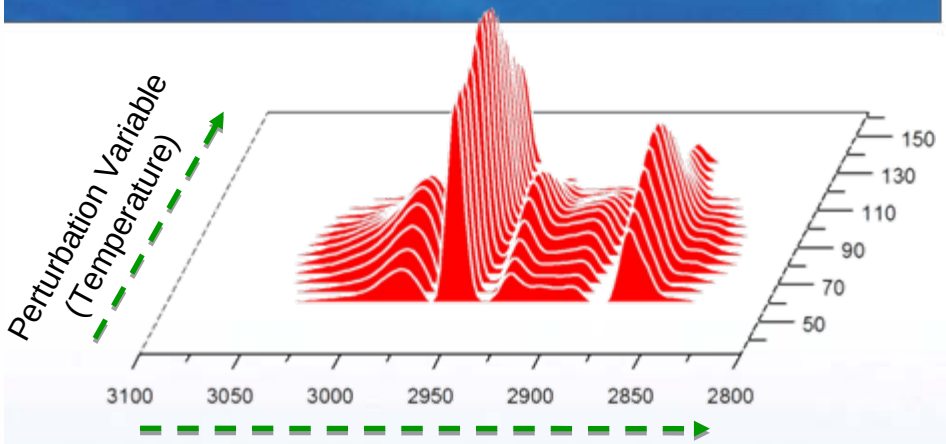
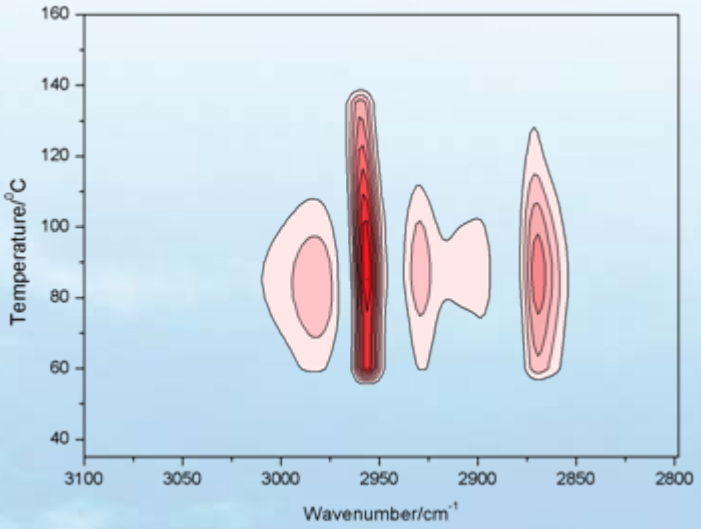
Perturbation Correlation Moving Window







Acquisition of Moving Window Spectra

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Perturbation Correlation Moving Window

Introduce external perturbation variable into correlation equations

【MW2D】

MW2D (based on an auto-correlation):

$$\Omega_j(v,p_j)=\frac{1}{2m}\sum_{J=j-m}^{j+m}\tilde{y}_j{}^2(v,p_J)$$

MW2D (based on horizontal slice spectra):

$$\Omega_{\Phi,j}(v,p_j)=\frac{1}{2m}\sum_{J=j-m}^{j+m}\tilde{y}_j(v,p_J)\cdot\tilde{y}_j(v_c,p_J)$$

$$\Omega_{\Psi,j}(v,p_j)=\frac{1}{2m}\sum_{J=j-m}^{j+m}\tilde{y}_j(v,p_J)\cdot\sum_{K=j-m}^{j+m}M_{JK}\cdot\tilde{y}_j(v_c,p_K)$$

【PCMW2D】

PCMW2D (synchronous):

$$\Pi_{\Phi,j}(v,p_j)=\frac{1}{2m}\sum_{J=j-m}^{j+m}\tilde{y}(v,p_J)\cdot\tilde{p}_J\sim\left(\frac{\partial y}{\partial p}\right)_v$$

PCMW2D (asynchronous):

$$\Pi_{\Psi,j}(v,p_j)=\frac{1}{2m}\sum_{J=j-m}^{j+m}\tilde{y}(v,p_J)\cdot\sum_{K=j-m}^{j+m}M_{JK}\cdot\tilde{p}_K\sim-\left(\frac{\partial^2 y}{\partial p^2}\right)_v$$

Morita, S.; Shinzawa, H.; Noda, I.; Ozaki, Y. *Applied Spectroscopy* **2006**, 60, 398-406.

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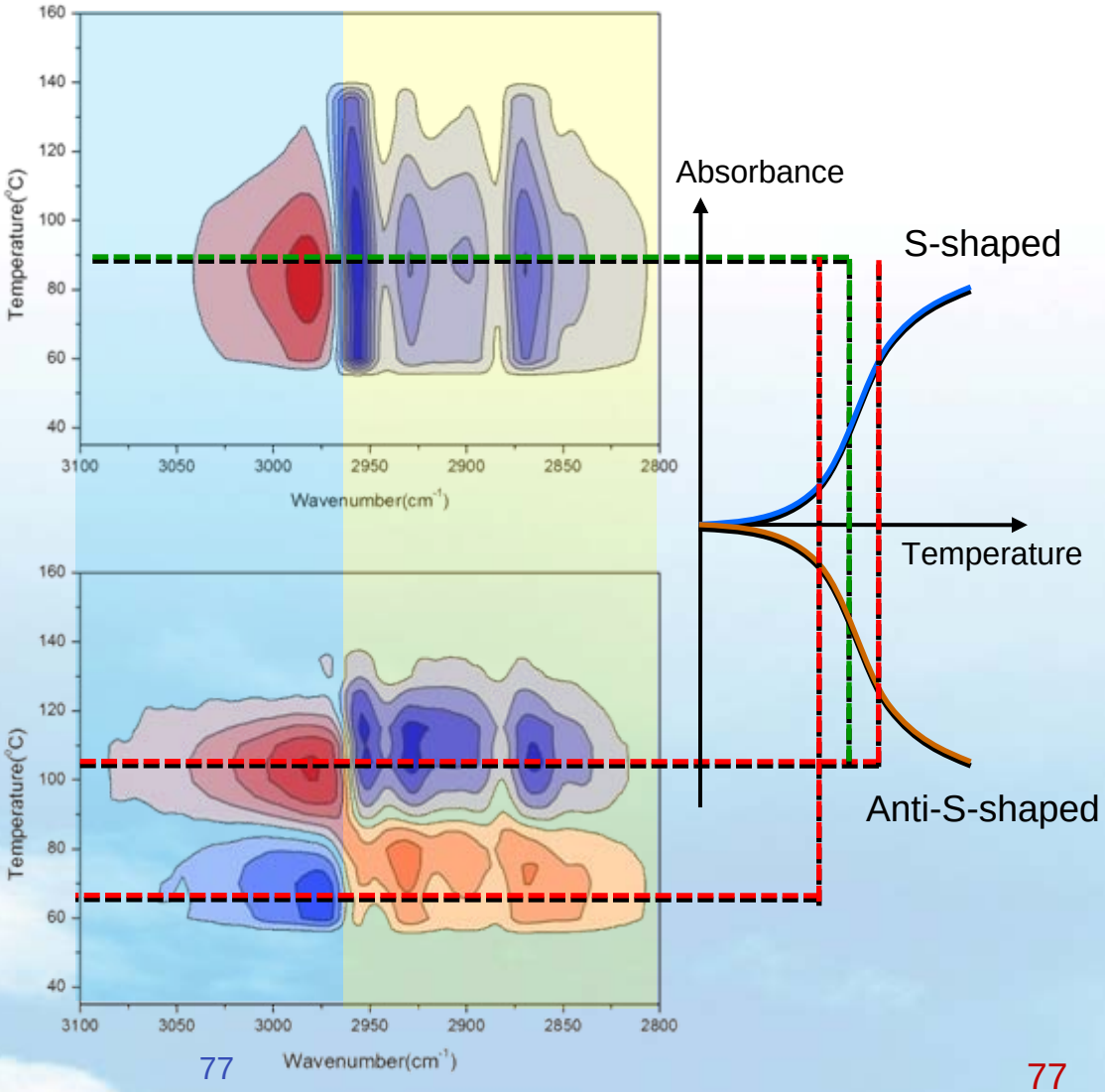
Perturbation Correlation Moving Window

【Rules of PCMW2D】

Synchronous	Asynchronous	Spectral Change
+	+	↗
+	0	→
+	−	↘
0	+	↷
0	0	⟶
0	−	↘
−	+	↙
−	0	↶
−	−	↙

(In the case of liner increment perturbation)



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Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

Main chain LCP

Rigid chain → High strength and modulus ↔ Polycondensation — USA

Mesogen-Jacketed LCP

Side chain LCP

Flexible chain → Photoelectronic response ↔ Polyaddition — Germany

Molecular structure of MJLCP

Only a covalent linkage or a short spacer

Δ

Amorphous state

The flexible main chains are constrained to take an extended chain conformation

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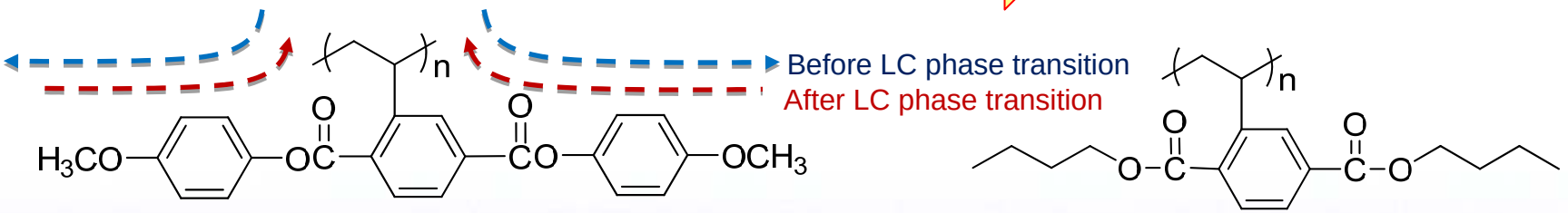
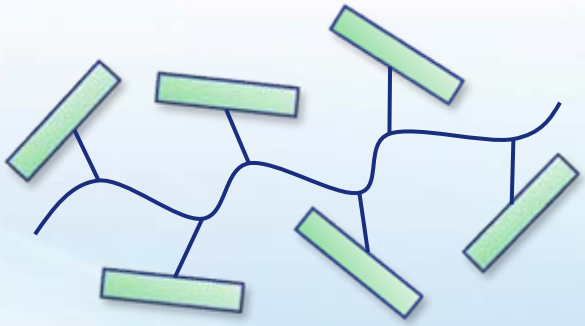
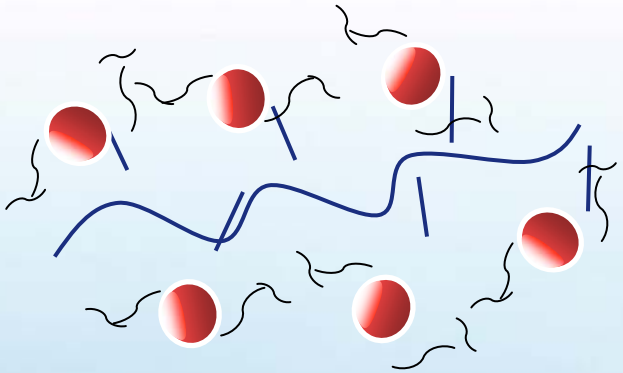
Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

PMPCS → PDBVT







Rigid side groups

Flexible side groups

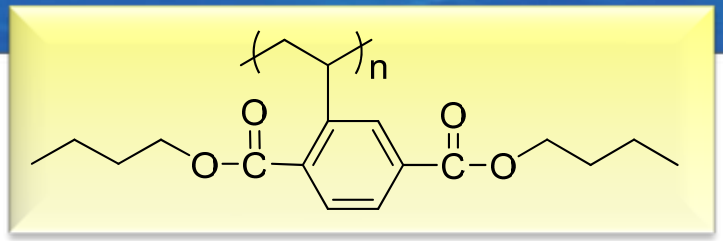
Mechanism?

Nematic phase

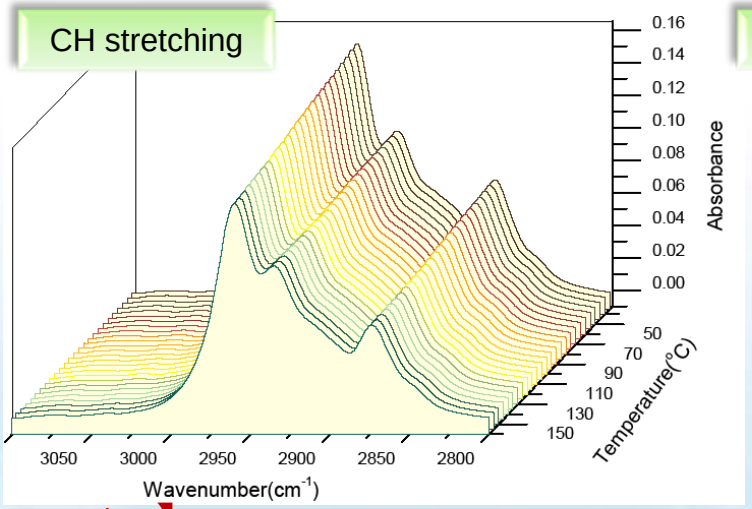
2D hexagonal columnar phase

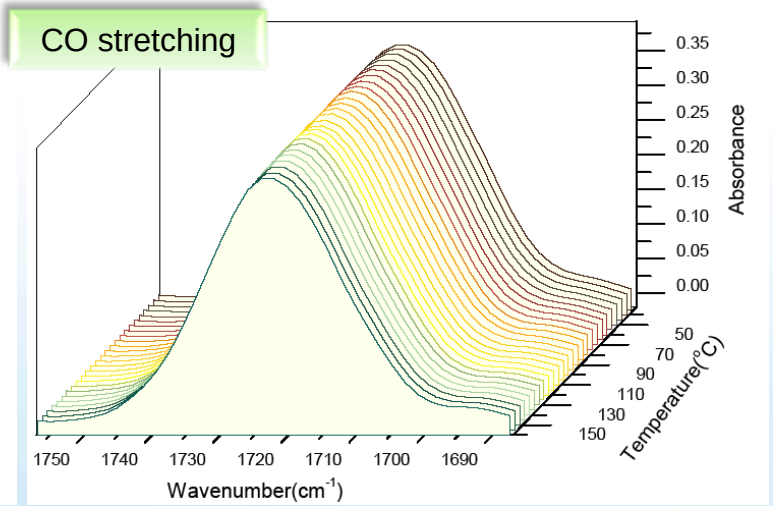
1. Shen, Y.; Wu, P. Y.; Noda, I.; Zhou, Q. F. *J. Phy. Chem. B* ***2005,*** 109, 6089-6095.
2. Yin, X. Y.; Wan, X. H.; Cheng, S. Z. D.; Zhou, Q. F. *J. Am. Chem. Soc.* **2003**, 125, 6854.

Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

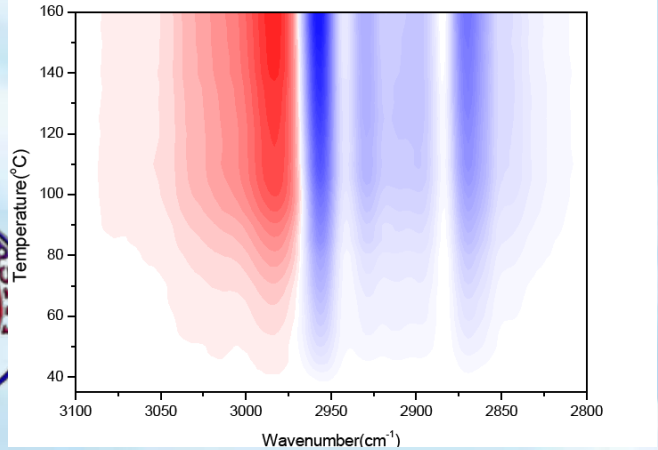


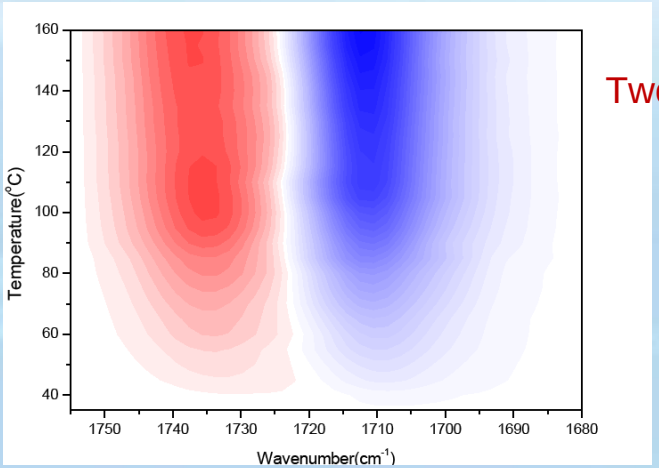
【Conventional IR spectra】





【Differential spectra】 (reference spectrum: 35 °C)





Two splitting bands

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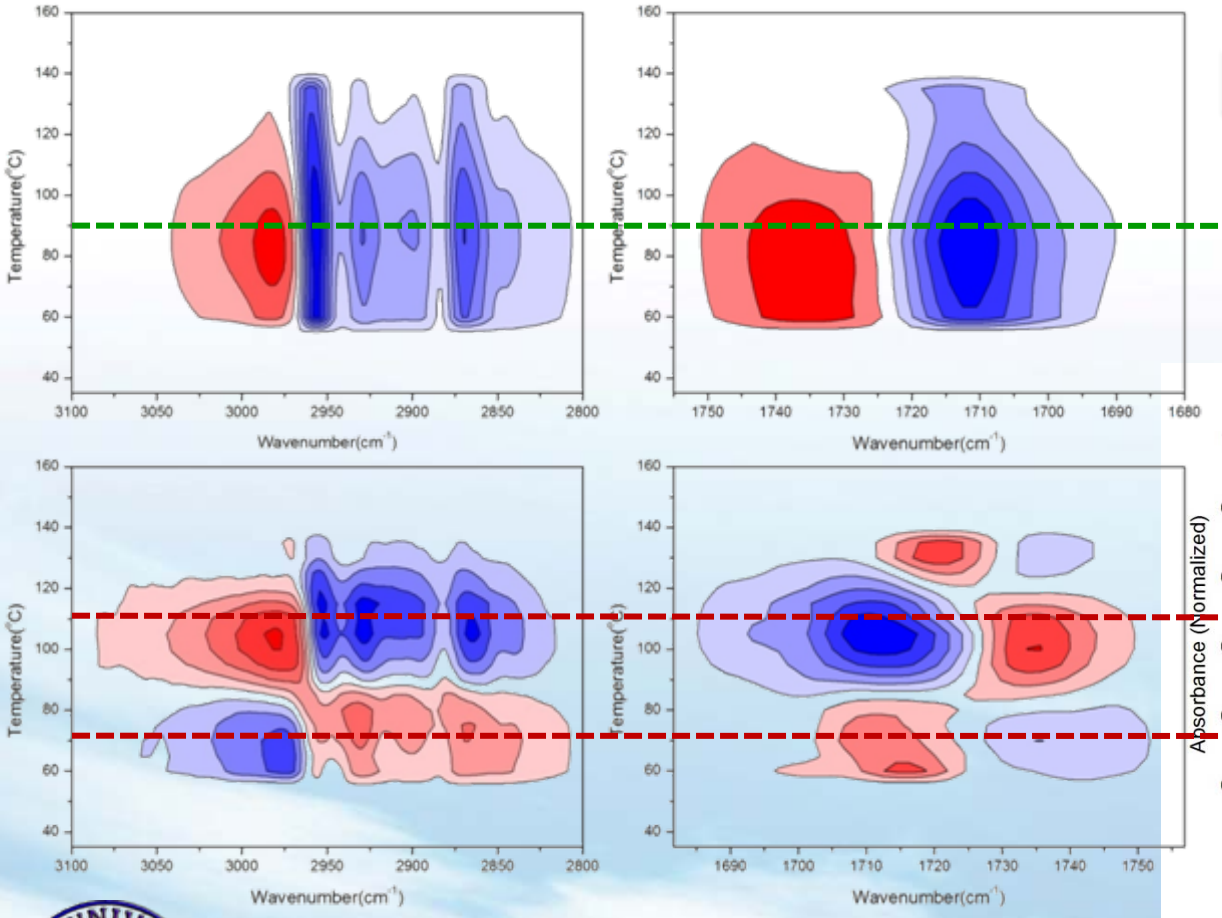
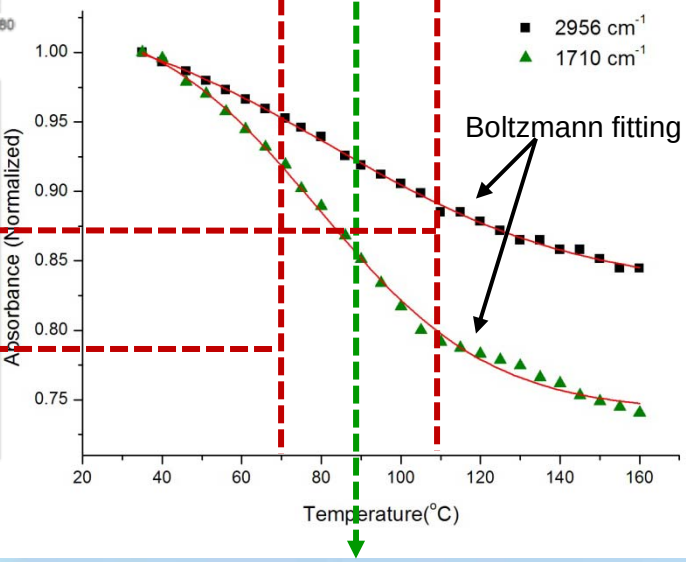
Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

【Perturbation Correlation Moving Window】



LC phase development: 70~110 °C



DSC: no observable LC phase transition

WAXD: 100 °C

LC phase transition: ≈90 °C

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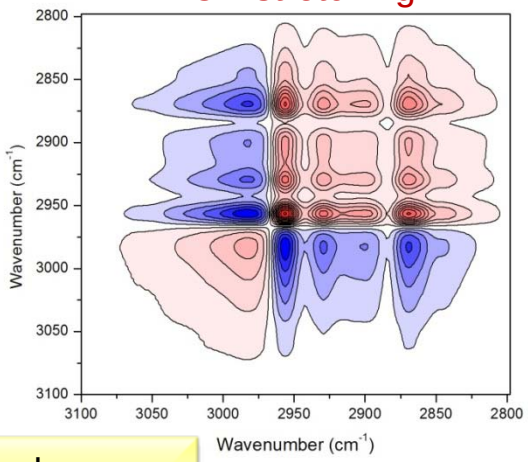
Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

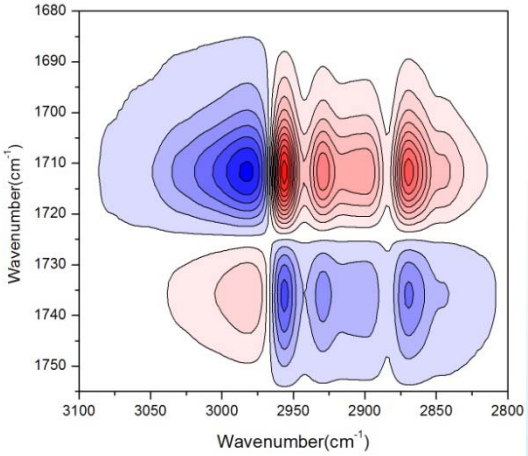
【2D Correlation Spectra】(70~110 °C)

Synchronous

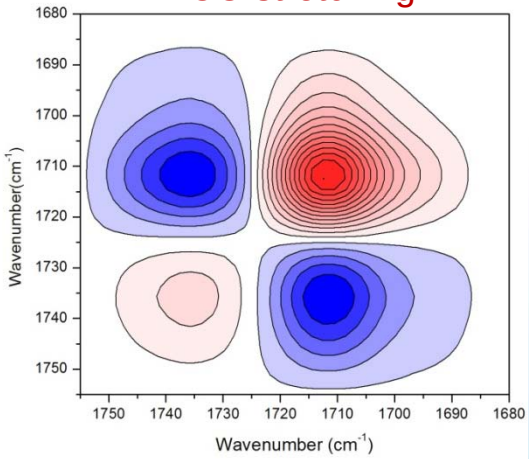
CH stretching



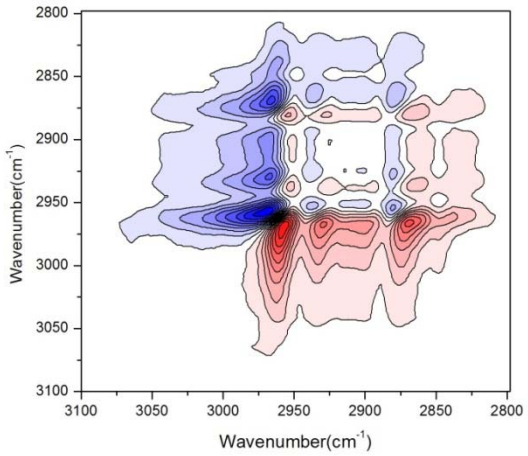
CH & CO

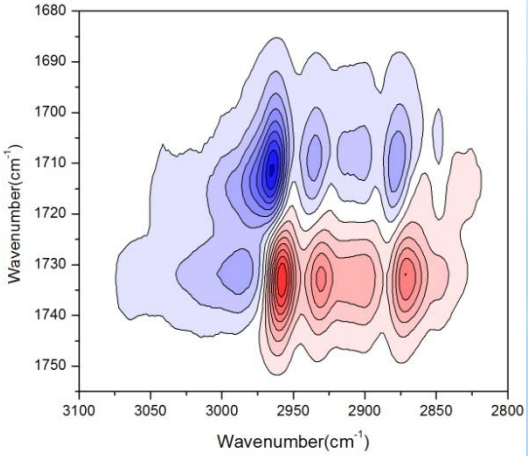


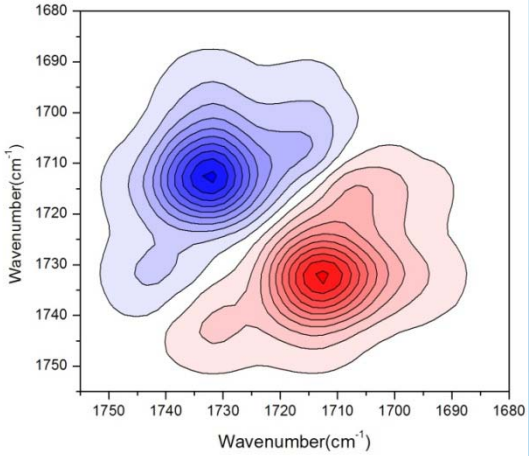
CO stretching



Asynchronous







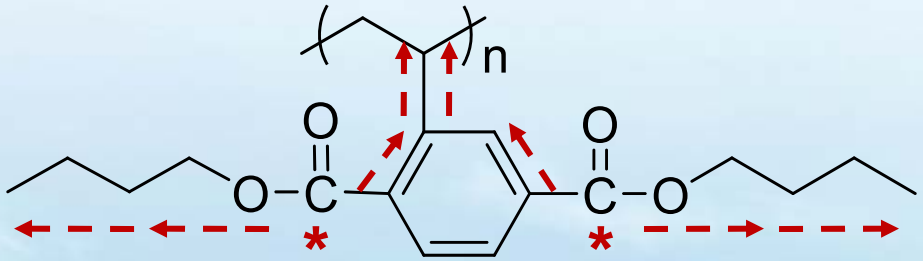
Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

Specific order (70~110 °C)

1732 > 2837 > 3041, 2987 > 1710 > 1714 > 2871 > 2958 > 2900 > 2935

ν (CO)(1732) > $\nu_s(CH_2)$ > ν_{ar}, $\nu_{as}(CH_3)$ (disorder) > ν (CO)(1710) > ν (CO)(1714) > $\nu_s(CH_3)$ > $\nu_{as}(CH_3)$ > ν (CH) > $\nu_{as}(CH_2)$ (side chains)

CO → CH_2 → CH_3, phenylene → CH (backbone)



Carbonyl plays a key role in the formation of 2D hexagonal columnar phase !

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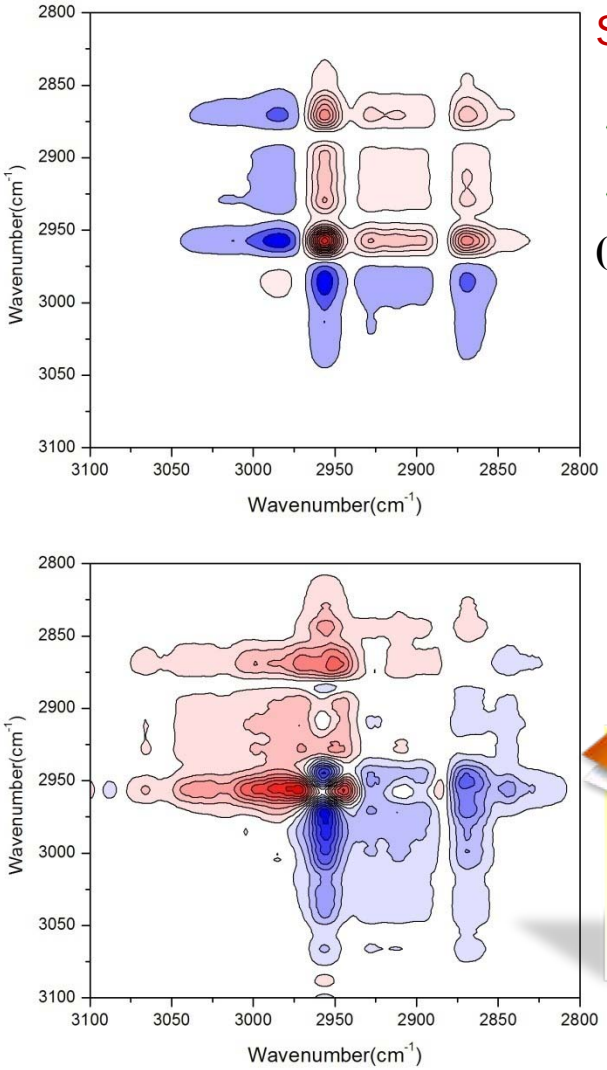
Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

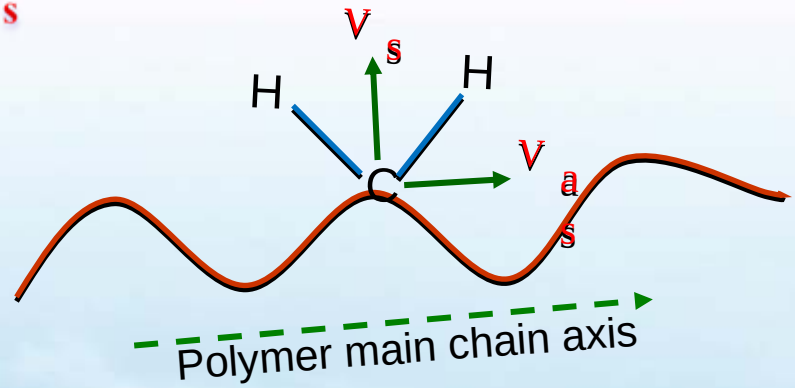
【2D Correlation Spectra】(35~65 °C)



Specific order (partial)

- $\nu_{as}(CH_3)$ (2956) > $\nu_{s}(CH_3)$ (2870)
- $\nu_{as}(CH_2)$ (backbone) (2913) > $\nu_{as}(CH_2)$ (side chains) (2931) > $\nu_{s}(CH_2)$ (2840)

$\nu_{as} > \nu_{s}$



The backbone and flexible side chains extended vertically before it twisted laterally preparing for the formation of 2D hexagonal columnar phase !

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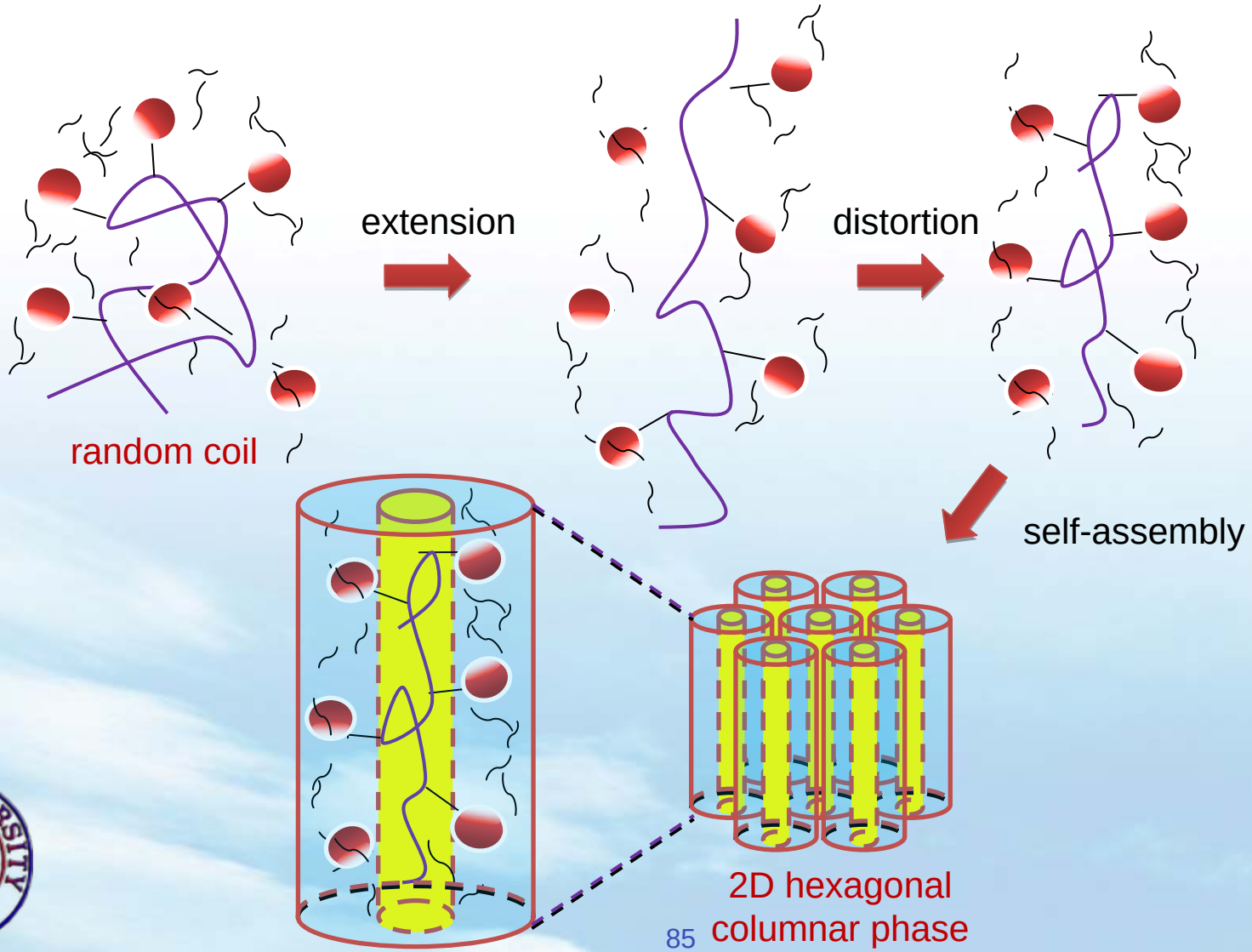
Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

【Mechanism】



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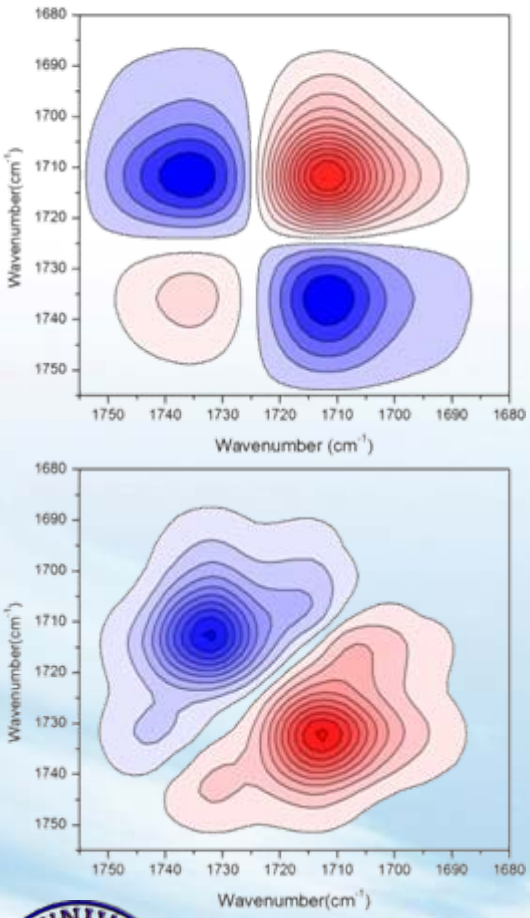
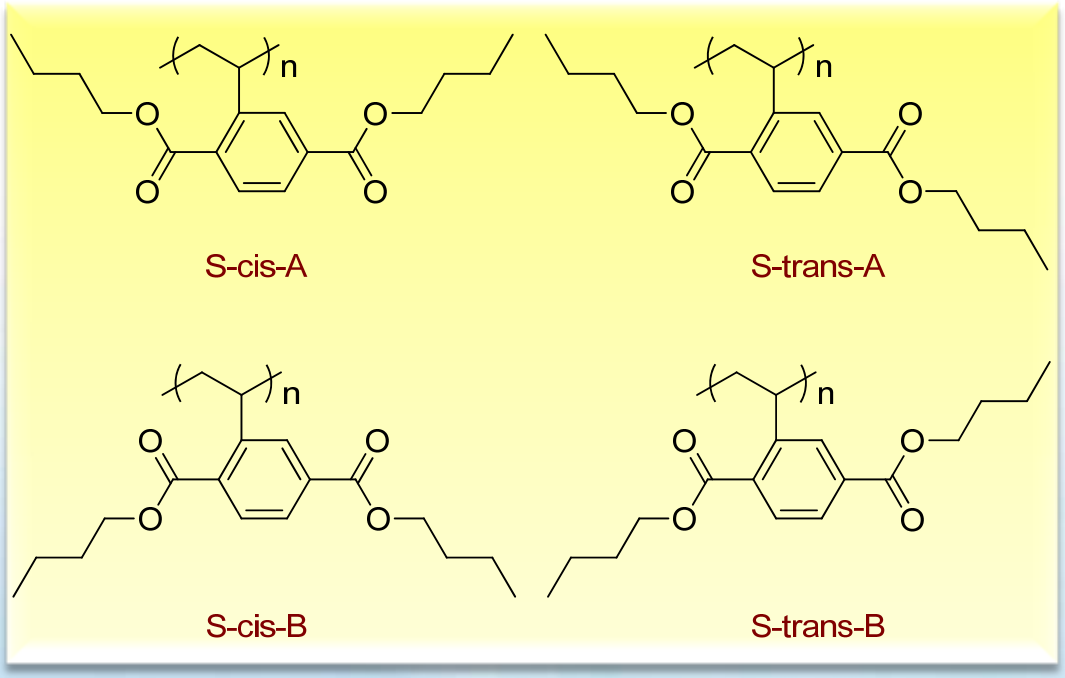
Supramolecular Self-Assembly Thermodynamic Mechanism of PDBVT

【CO splitting phenomenon】



Four splitting peaks: 1707, 1712, 1731, 1741



Further investigations

- The assignment of four splitting peaks to different conformers
- The influence of carbonyl conformation transition on the formation of 2D hexagonal columnar phase

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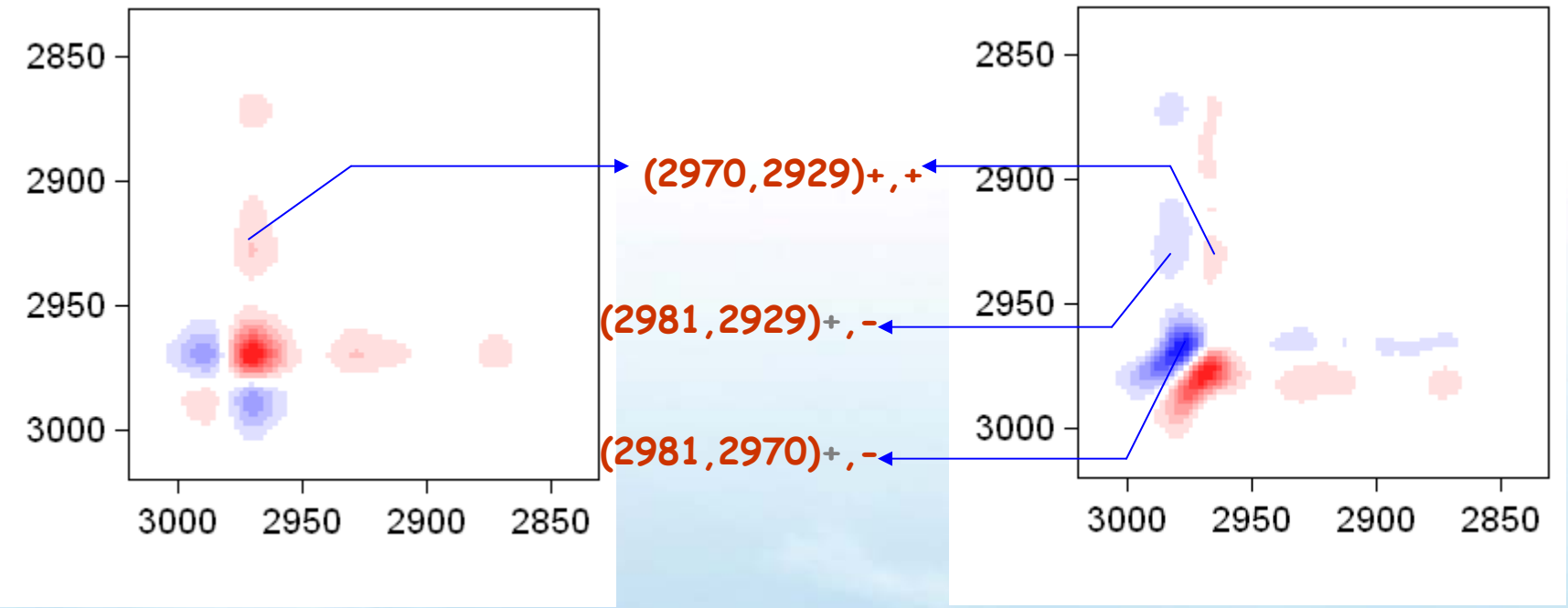
【Acknowledge】

NSFC


Acknowledgement: NSFC(20425415)
Professor H. W. Siesler
and Dr. Isao Noda for helpful discussion

Thank You !

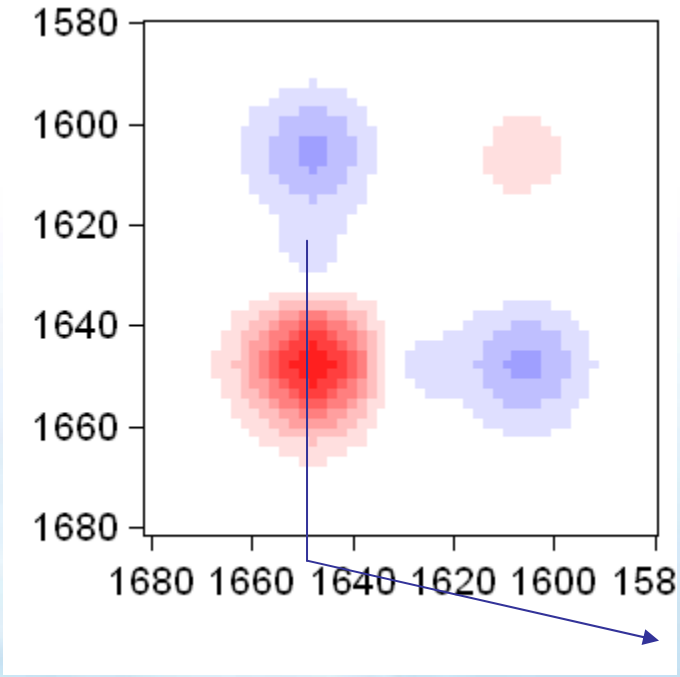
Investigation of CH Bands during cooling- 2DIR

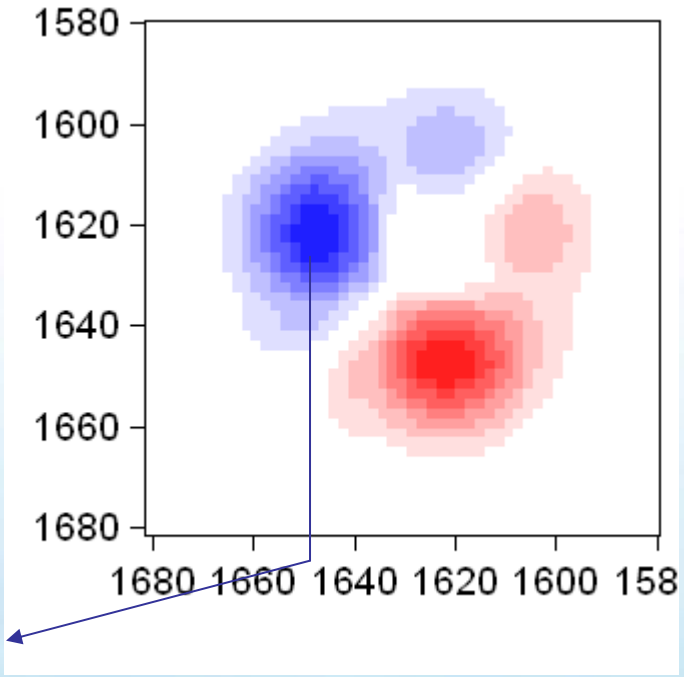


2970 > 2929 > 2981

CH_3 with less water > main-chain $\nu_{as}(CH_2)$ > CH_3 with more water

Investigation of Amide I Band during cooling- 2DIR



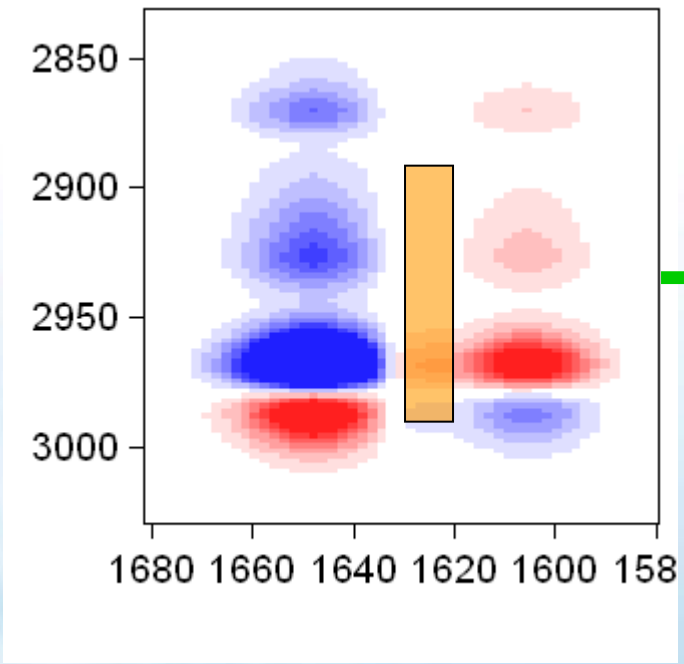


(1649,1624)-,-

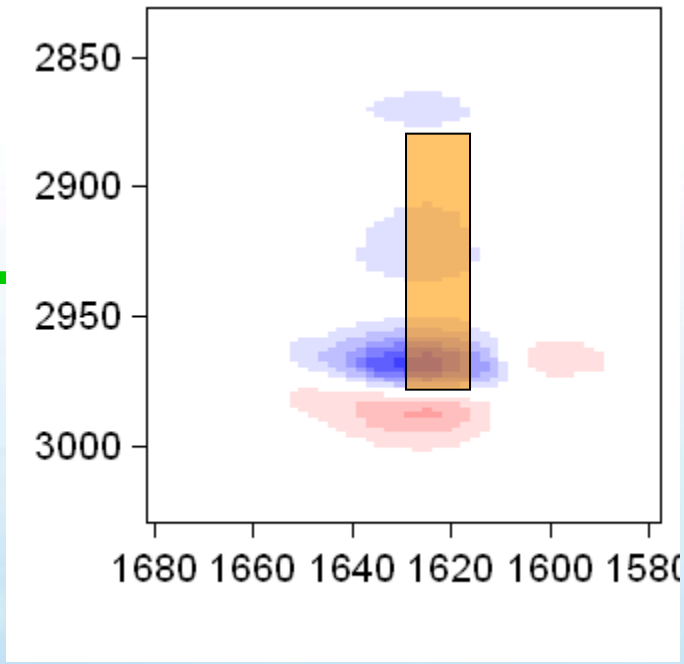
1649> 1624

C=O···D-N > C=O···D-O-D

Investigation of CH vs. Amide I region in cooling-2DIR



(1624,2981)-,-
(1624,2970)-,-
(1624,2929)-,-



1649 > 1624 > 2970 > 2929 > 2981

C=O with D-N > C=O with water > CH_3 with less water > main-chain ν as(CH_2) > CH_3 with more water

Dynamics mechanism of PNIPAM 20wt% D_2O solution during cooling

C=O with D-N > N-D with water > C=O with water

> CH_3 with less water > main-chain $\nu_{as}(CH_2)$ > CH_3 with more water