Physicochemical investigation of phosphoric acid doped poly(2,5-benzimidazole) as electrolyte membrane for fuel cells

A. Majerus[1], F. Conti[1,2], C. Korte[1], W. Lehnert[1,3] and D. Stolten[1,4]

[1] Forschungszentrum Jülich GmbH, Institute for Energy Research – Electrochemical Process Engineering (IEK-3), 52425 Jülich, Germany

[2] Department of Chemical Sciences, University of Padova, Via Marzolo 1, 35131 Padova, Italy

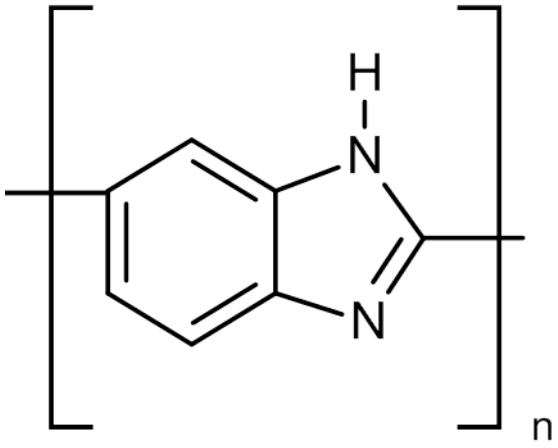
[3] Modeling in Electrochemical Process Engineering, RWTH Aachen University, Germany

[4] Chair for Fuel Cells, RWTH Aachen University, Germany

Outline

- Introduction
- Conductivity of doped ABPBI
- Pecularities of phosphoric acid
- Thermogravimetric analysis of phosphoric acid and doped ABPBI
- Raman spectroscopic investigation of doped ABPBI
- Summary

Introduction



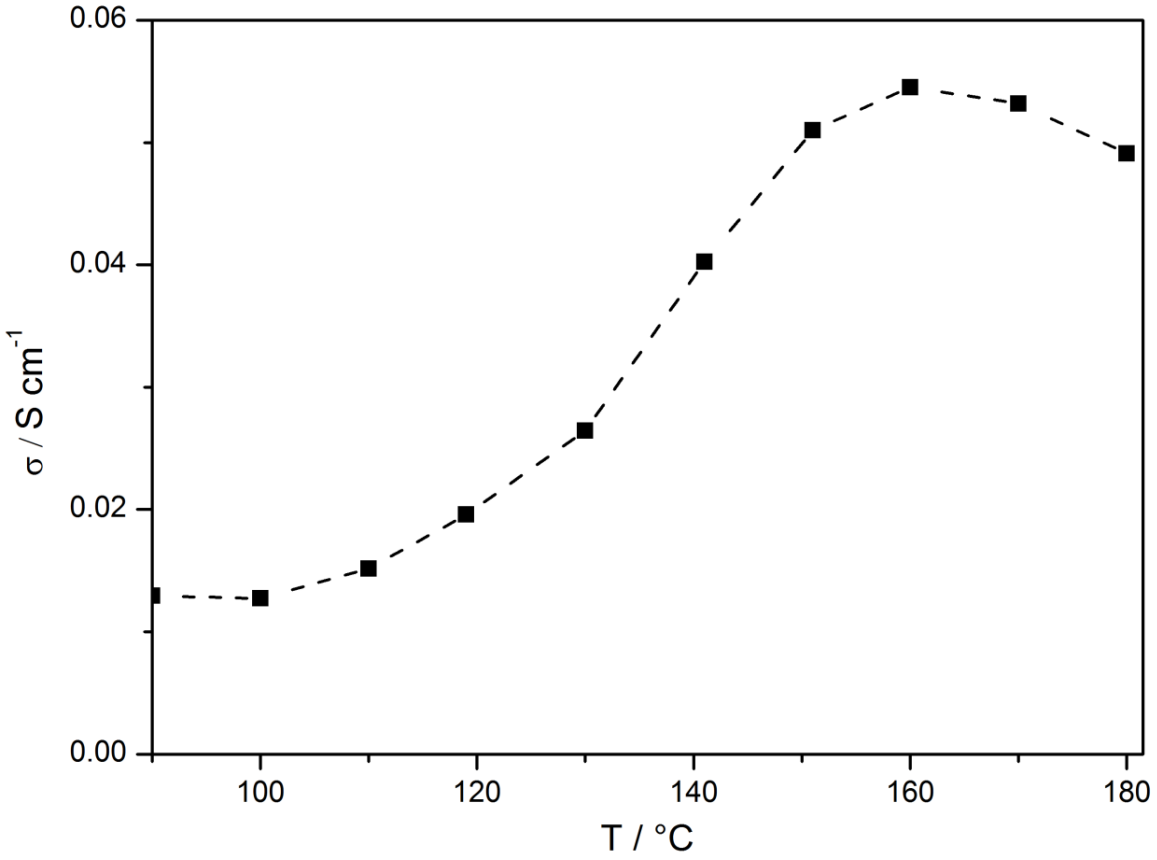
Membrane

- ABPBI: poly(2,5-benzimidazole)
- Crosslinked
- Exact structure FuMA-Tech (Germany) confidential

Doping process:

1. Membrane is dried to eliminate solvent remains
2. Membrane is immersed into hot acid (110 °C) in an open system for approx. 16 h
3. After doping, the surface of the membrane is dried with tissues

Proton conductivity of ABPBI membrane



Overlap of two different effects:

- Increase in conductivity with temperature increase
- Decrease in conductivity due to the dehydration of phosphoric acid
- Maximum at 160 °C

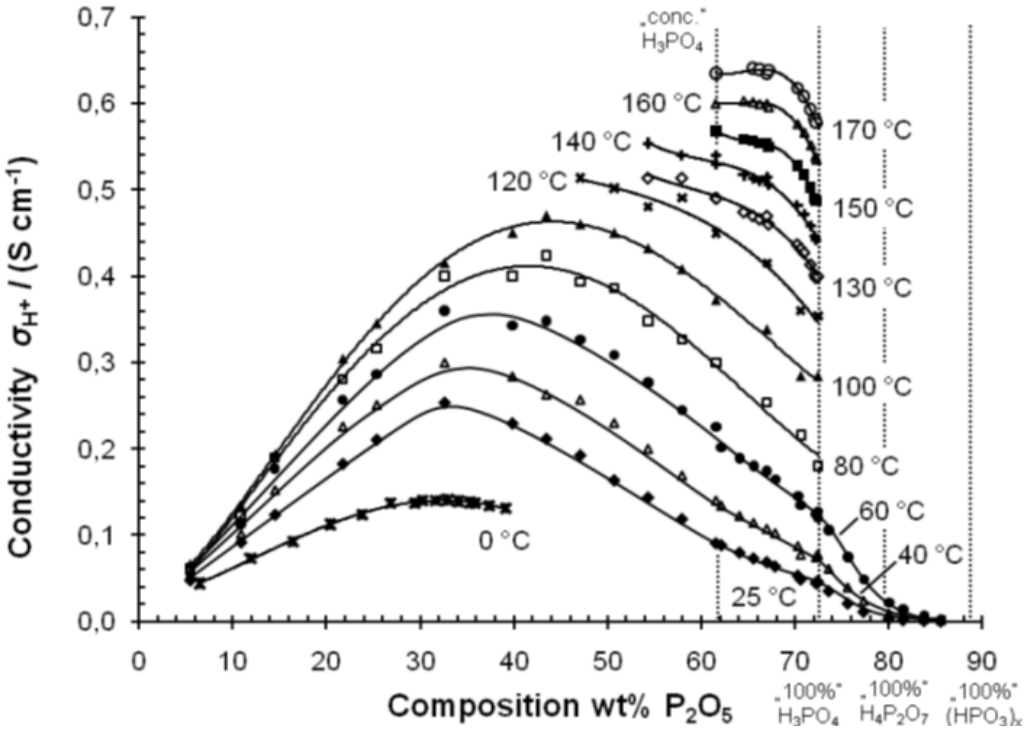
- *Constant dew point of ca. 13 °C, no humidification*
- *330 wt% phosphoric acid*

Shift of the equilibrium to the less conductive pyrophosphoric acid

$$2\ H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$

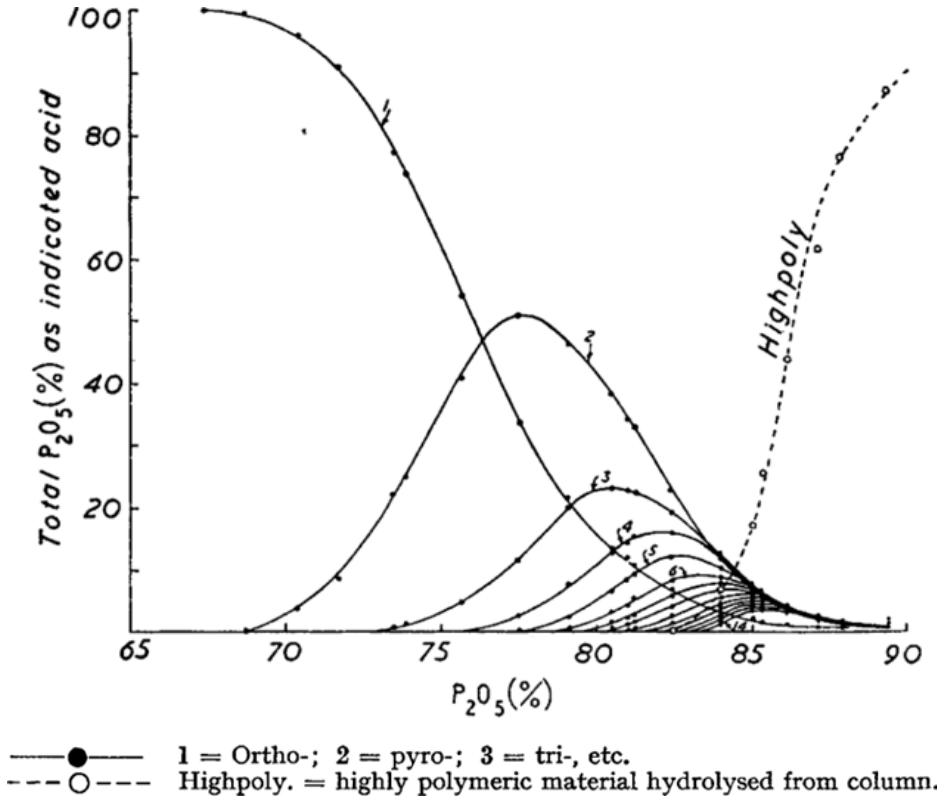
Pecularities of phosphoric acid

- Conductivity of phosphoric acid



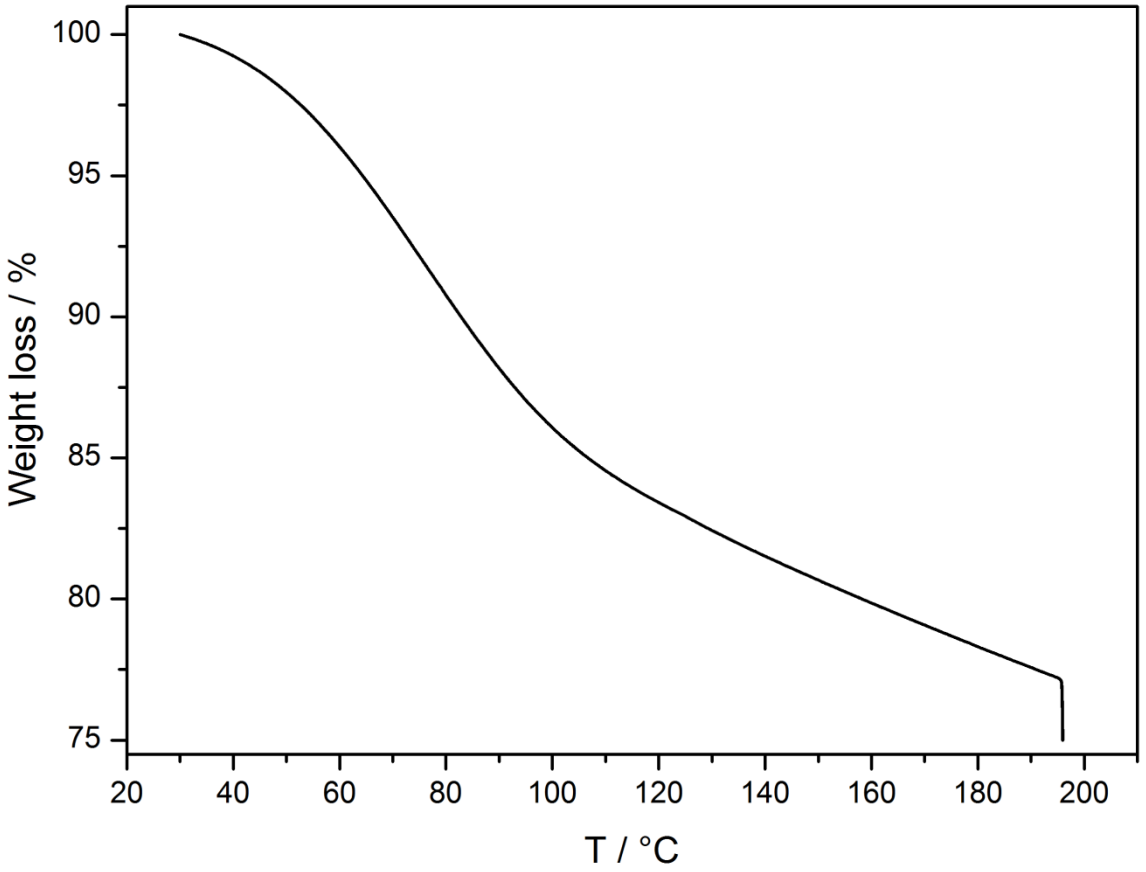
C. Korte, in Fuel Cell Science and Engineering, Vol. 1, ed.: D. Stolten, B. Emonts, Wiley-VCH, Weinheim

- Composition of phosphoric acid



R. F. Jameson, J. Chem. Soc 1 (1959) 752-759

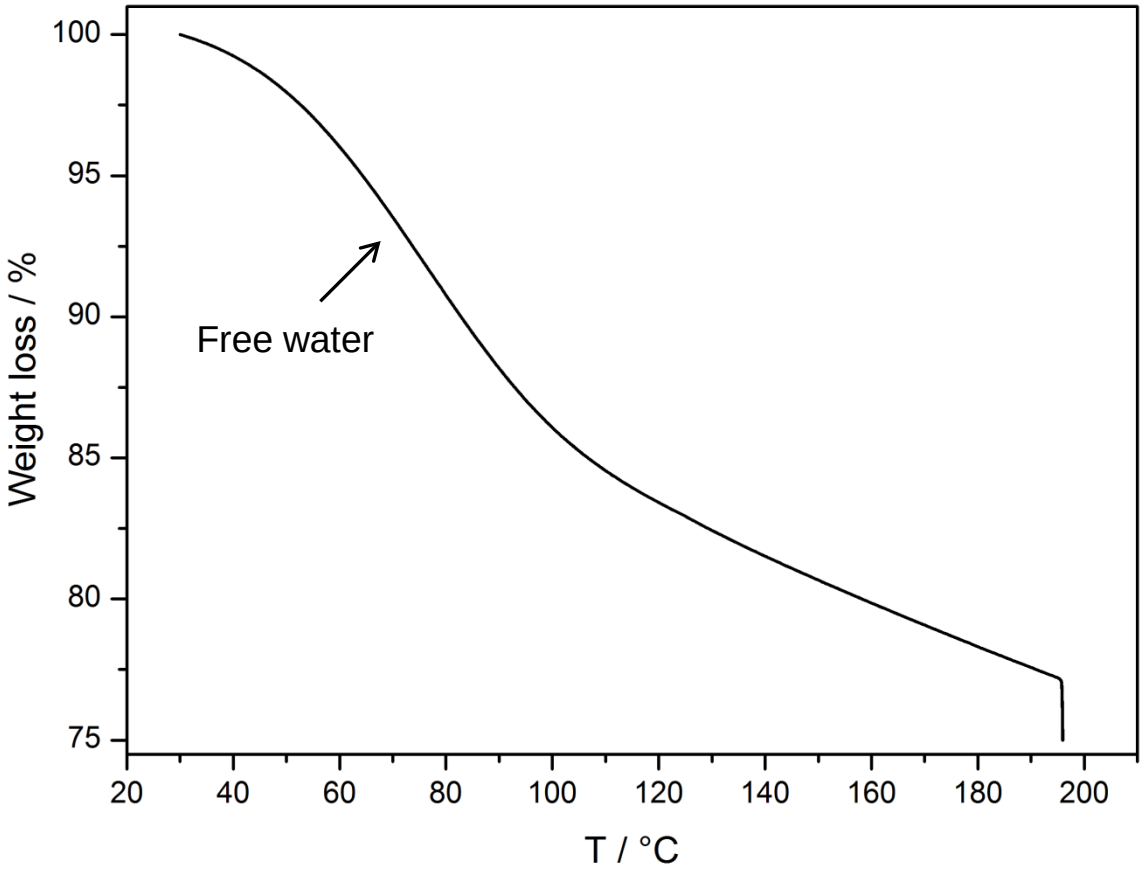
Thermogravimetric analysis of phosphoric acid



- *85 % phosphoric acid*
- *Heating rate 1 K/min*
- *One hour equilibration at 200 °C*
- *Atmosphere 50 ml/min dry N_2*

Thermogravimetric analysis of phosphoric acid

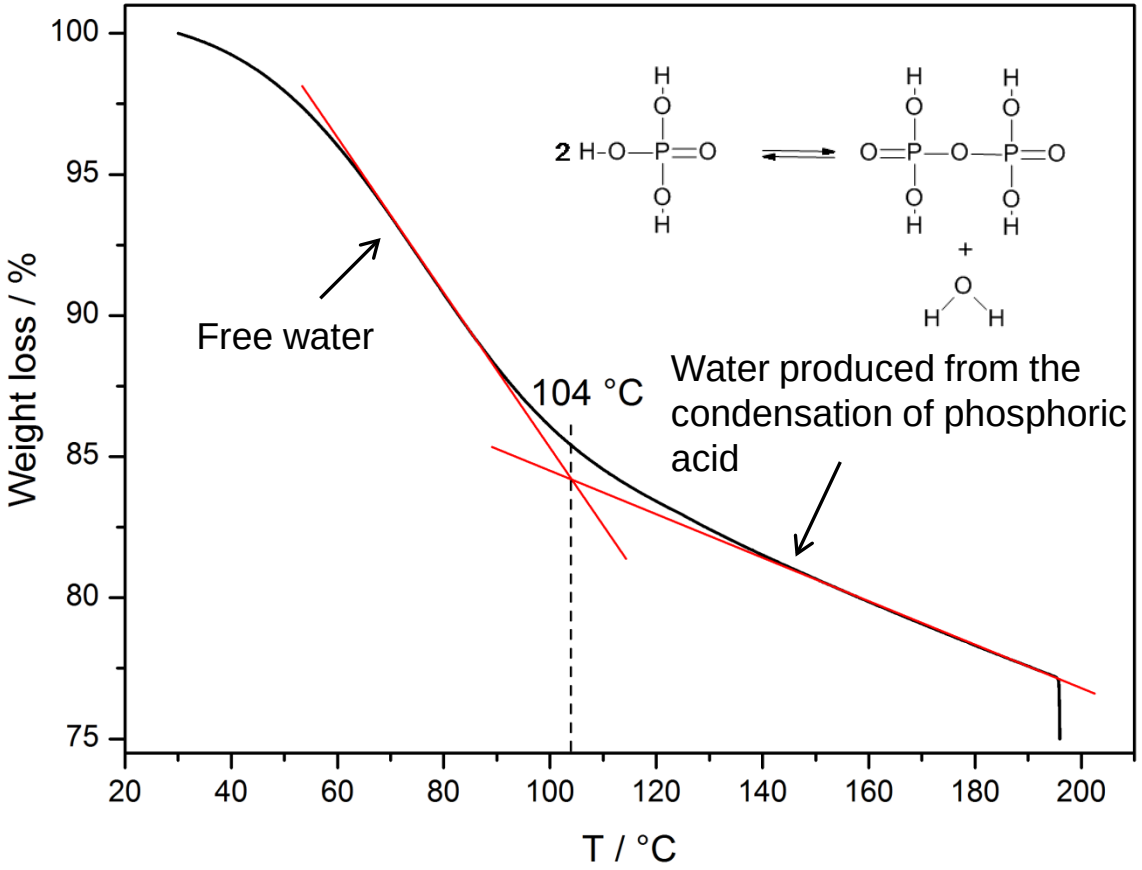
- First loss, 15 % → attributed to the evaporation of free water



- *85 % phosphoric acid*
- *Heating rate 1 K/min*
- *One hour equilibration at 200 °C*
- *Atmosphere 50 ml/min dry N_2*

Thermogravimetric analysis of phosphoric acid

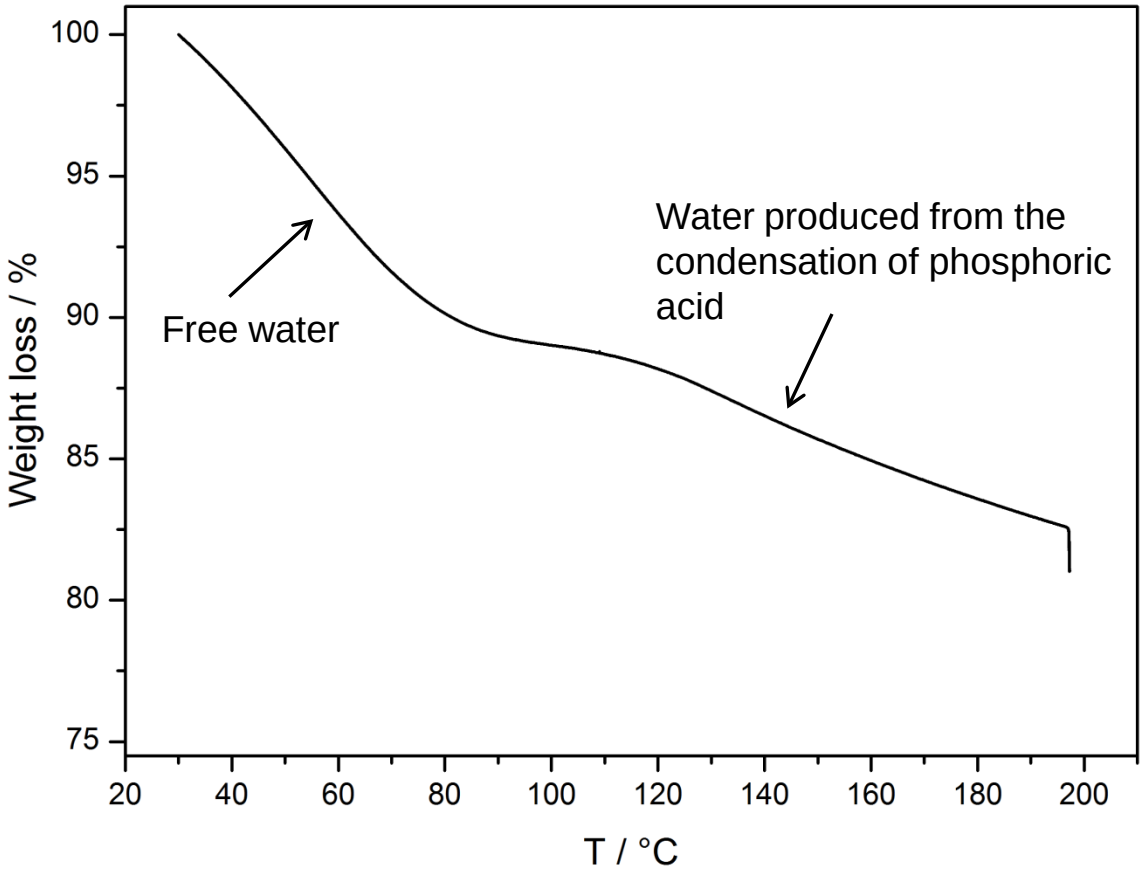
- First loss, 15 % → attributed to the evaporation of free water
- Second loss, 10 % → attributed to the condensation of phosphoric acid
- Second weight loss starts at about 104 °C



- *85 % phosphoric acid*
- *Heating rate 1 K/min*
- *One hour equilibration at 200 °C*
- *Atmosphere 50 ml/min dry N_2*

Thermogravimetric analysis of doped ABPBI

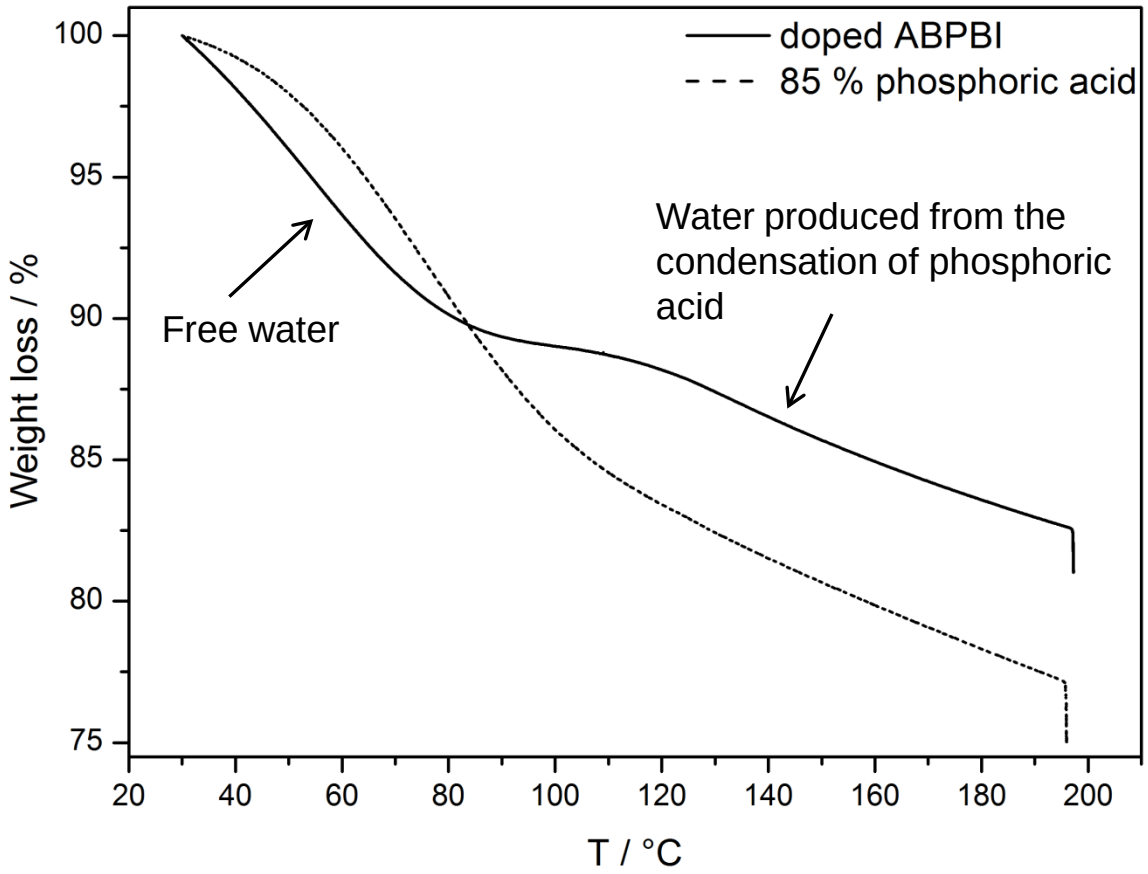
- First weight loss of 12 %
- Second weight loss of 8 % starts at about 117 °C



- *Crosslinked ABPBI*
- *356 wt% phosphoric acid*
- *Heating rate 1 K/min*
- *One hour equilibration at 200 °C*
- *Atmosphere 50 ml/min dry N_2*

Thermogravimetric analysis of doped ABPBI

- First weight loss of 12 %
- Second weight loss of 8 % starts at about 117 °C



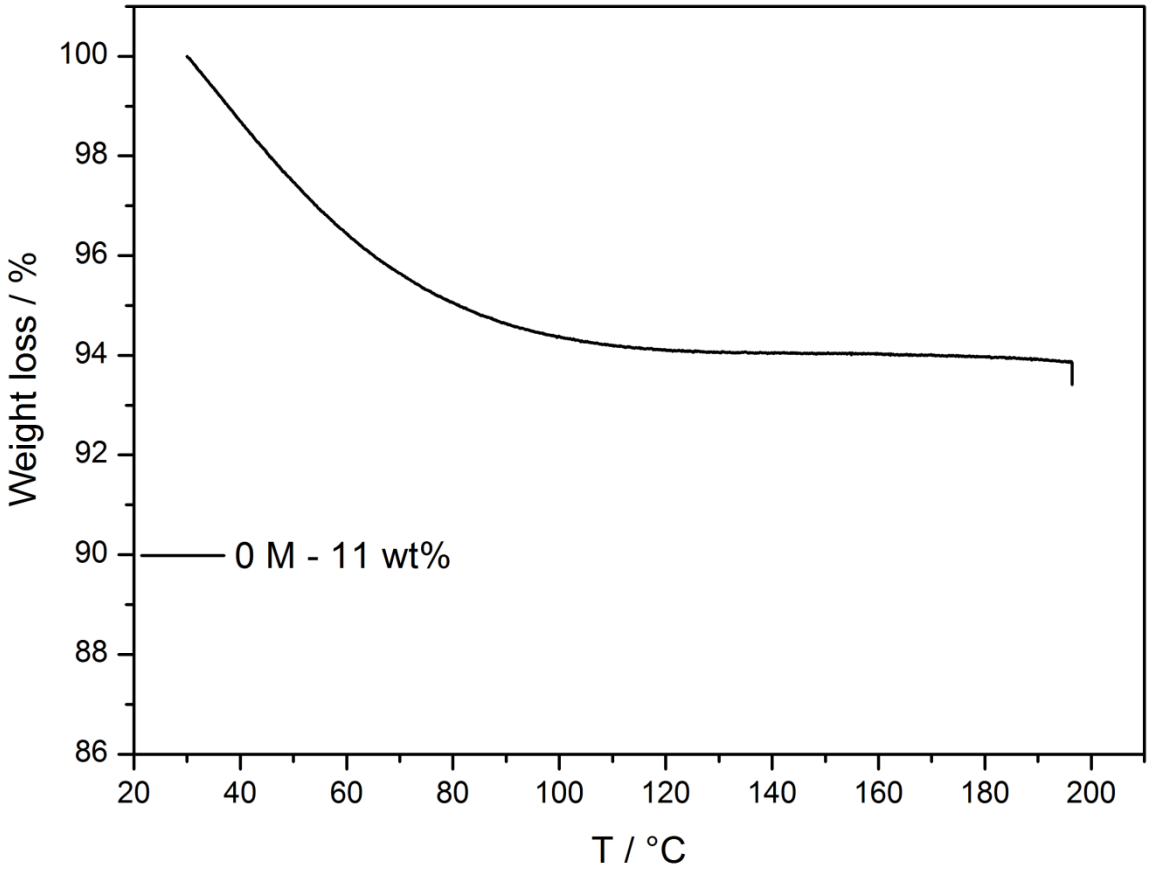
Main differences:

- First weight loss:
  15 % vs. 12 %
- Second weight loss:
  10 % vs. 8 %
- Condensation onset:
  104 °C vs. 117 °C
- Plateau in the spectrum of the doped membrane

- *Crosslinked ABPBI*
- *356 wt% phosphoric acid*
- *Heating rate 1 K/min*
- *One hour equilibration at 200 °C*
- *Atmosphere 50 ml/min dry N_2*

Thermogravimetric analysis of doped ABPBI

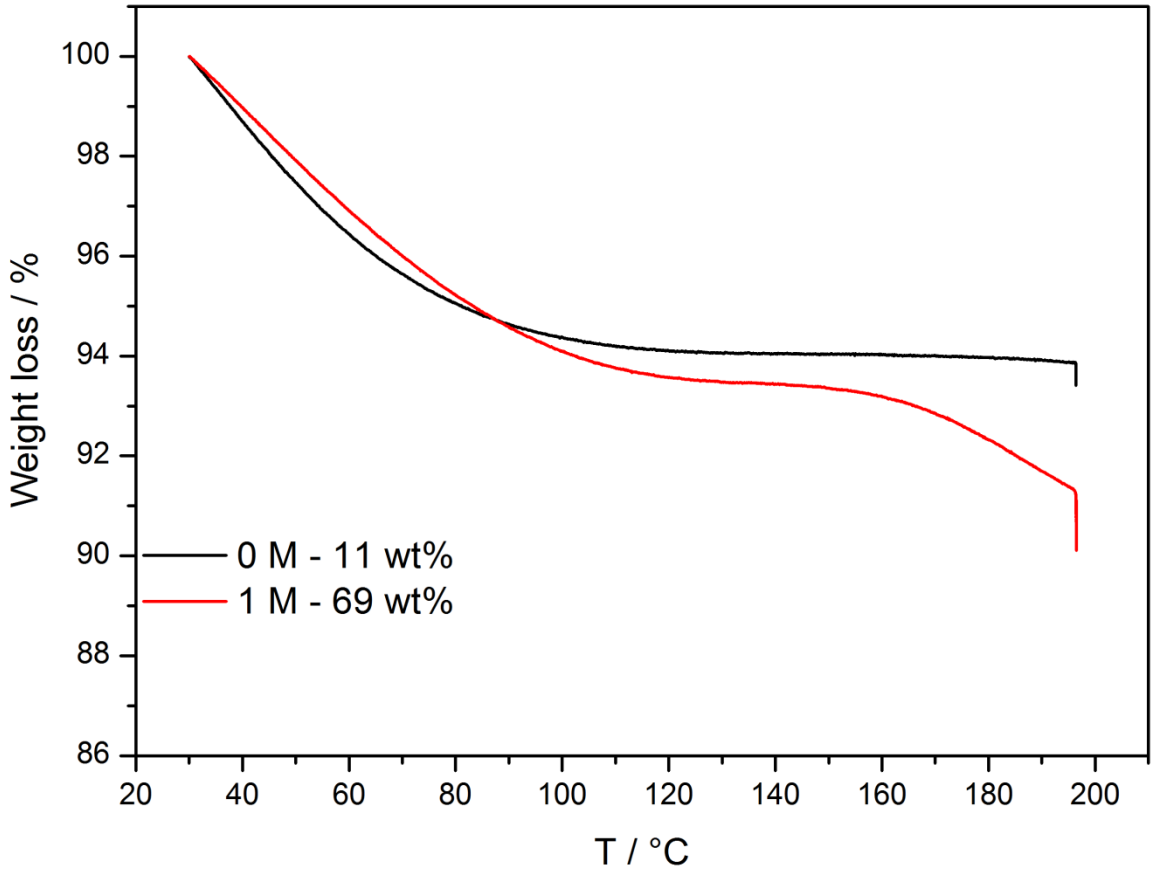
- ABPBI doped with different concentrations of phosphoric acid
- Different doping levels
- Different onset and end temperatures of plateau



- *Crosslinked ABPBI*
- *Doped for 6.5 h @ 80 °C*
- *Heating rate 1 K/min*
- *One hour equilibration at 200 °C*
- *Atmosphere 50 ml/min dry N_2*

Thermogravimetric analysis of doped ABPBI

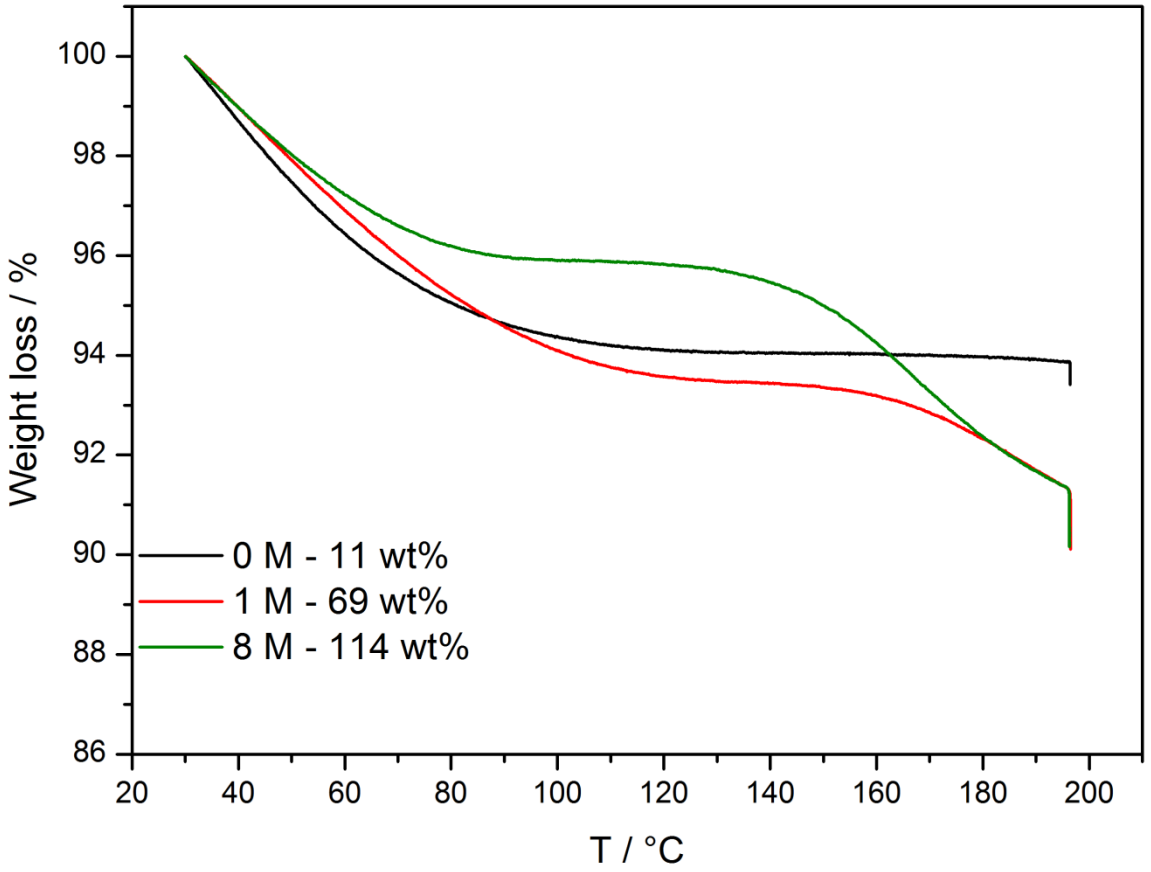
- ABPBI doped with different concentrations of phosphoric acid
- Different doping levels
- Different onset and end temperatures of plateau



- *Crosslinked ABPBI*
- *Doped for 6.5 h @ 80 °C*
- *Heating rate 1 K/min*
- *One hour equilibration at 200 °C*
- *Atmosphere 50 ml/min dry N_2*

Thermogravimetric analysis of doped ABPBI

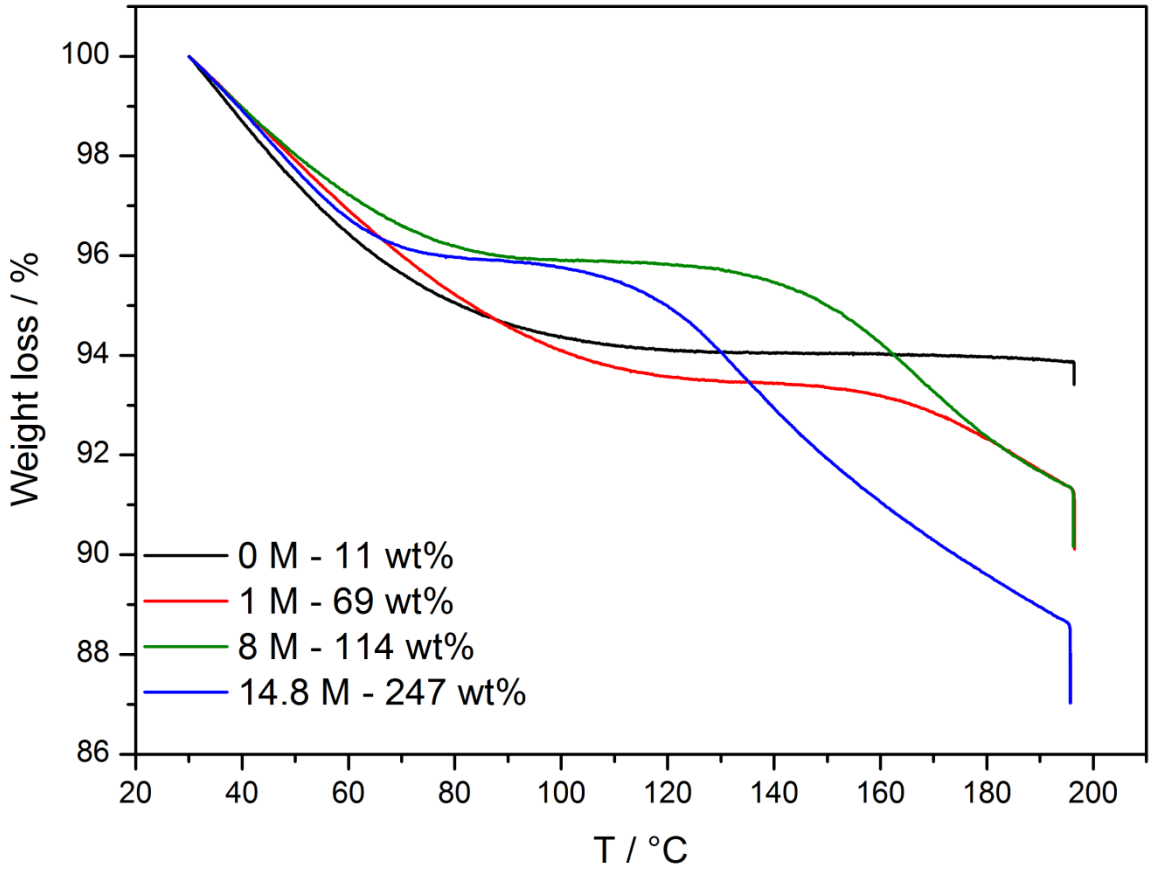
- ABPBI doped with different concentrations of phosphoric acid
- Different doping levels
- Different onset and end temperatures of plateau



- *Crosslinked ABPBI*
- *Doped for 6.5 h @ 80 °C*
- *Heating rate 1 K/min*
- *One hour equilibration at 200 °C*
- *Atmosphere 50 ml/min dry N_2*

Thermogravimetric analysis of doped ABPBI

- ABPBI doped with different concentrations of phosphoric acid
- Different doping levels
- Different onset and end temperatures of plateau



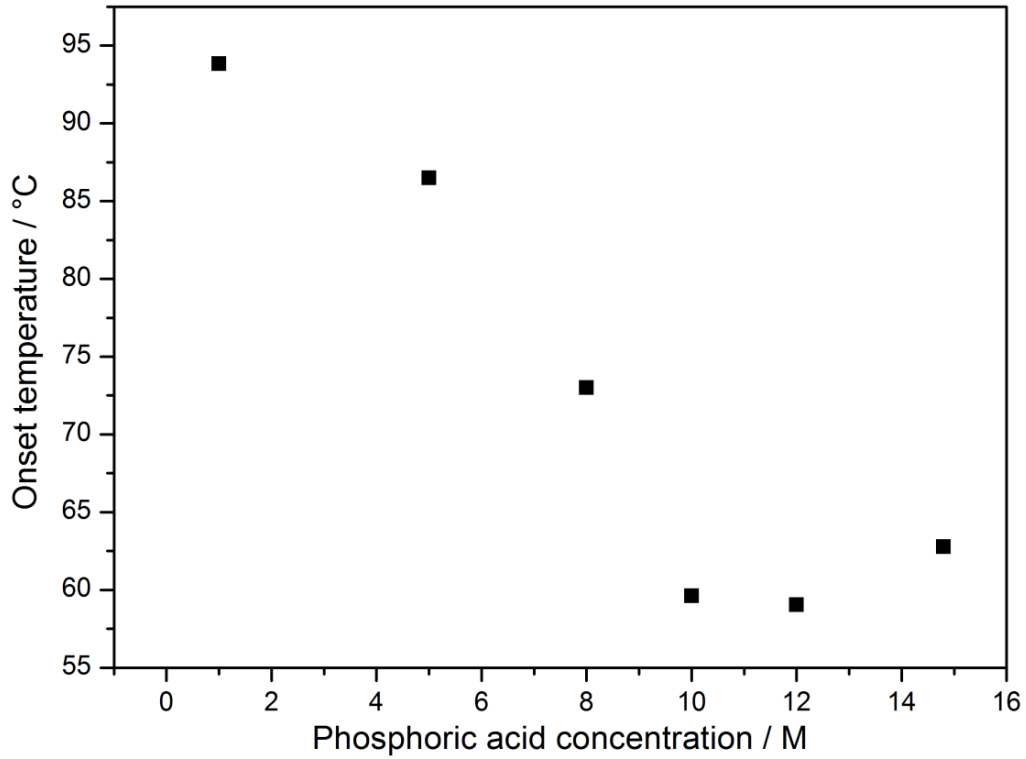
- *Crosslinked ABPBI*
- *Doped for 6.5 h @ 80 °C*
- *Heating rate 1 K/min*
- *One hour equilibration at 200 °C*
- *Atmosphere 50 ml/min dry N_2*

Focus on the plateau

Onset of the plateau

- Free water almost completely evaporated
- Temperature decreases with increasing concentration

  → less water in the membrane

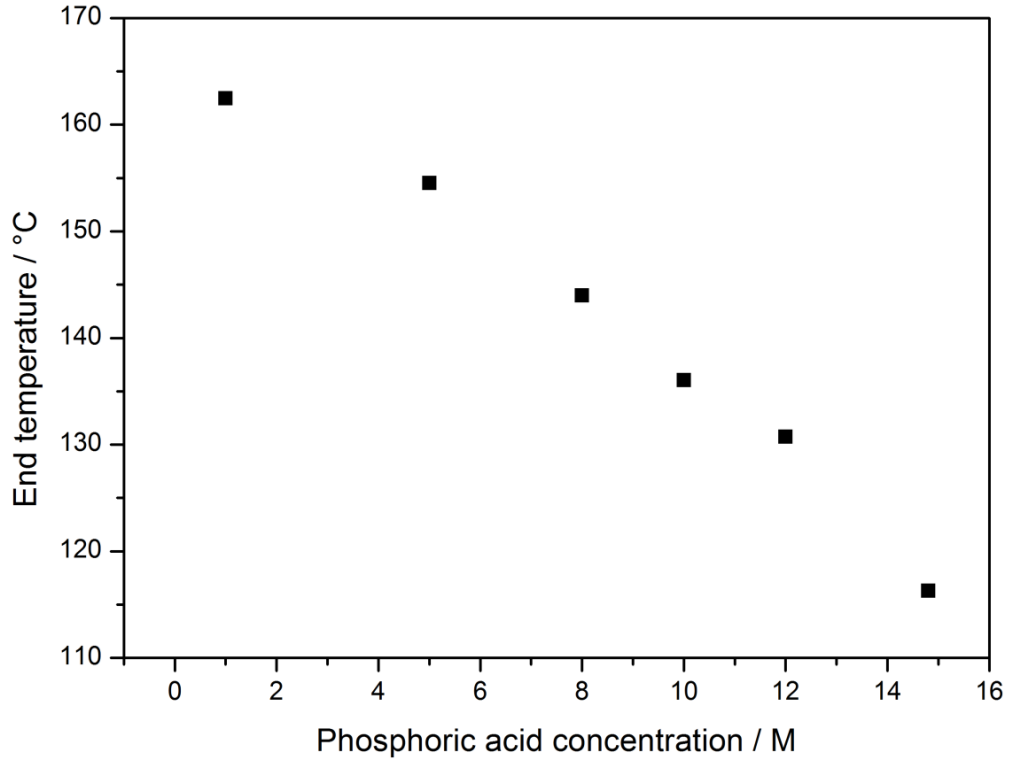


Focus on the plateau

End of the plateau

- Start temperature of condensation
- Temperature decreases with increasing concentration

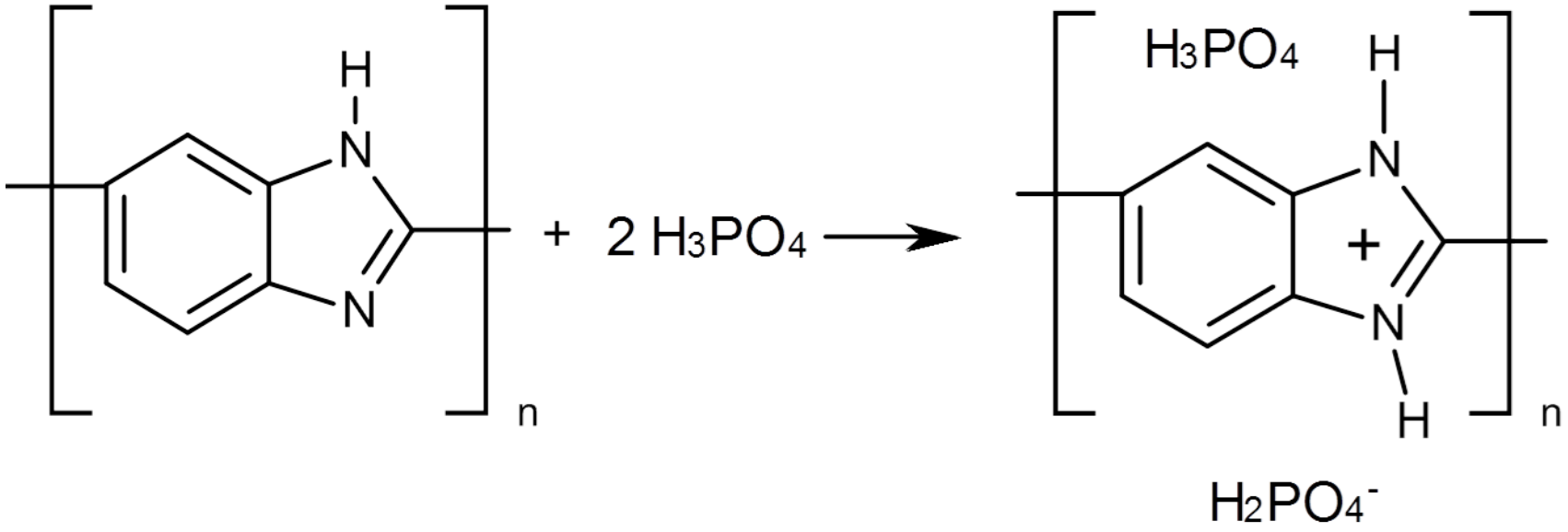
  → more acid in the membrane



Possible explanation for the thermal signal of doped ABPBI

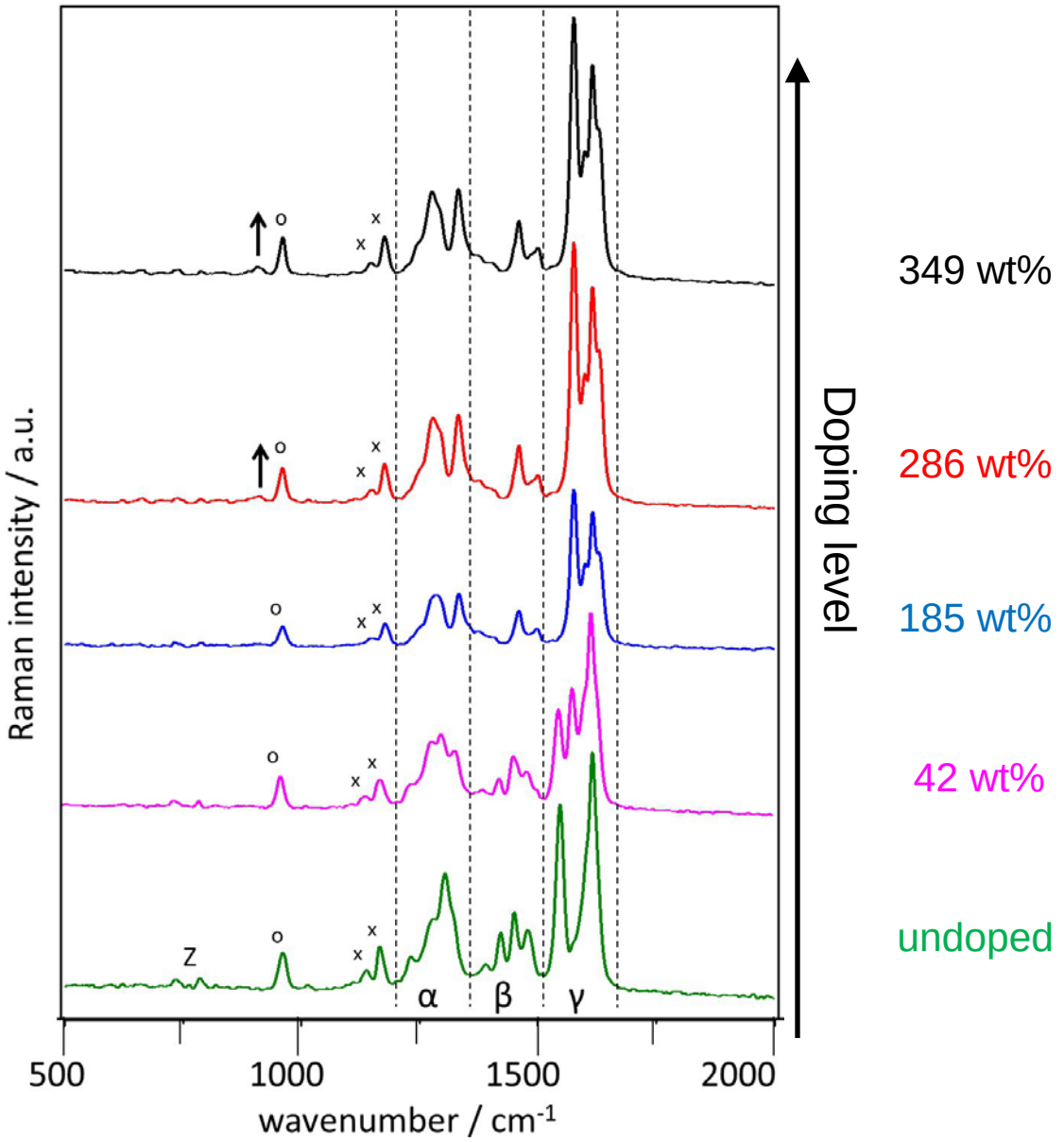
- 2 kinds of phosphoric acid: free and bound molecules
- Phosphoric acid protonates imidazole
- Bonds need to be broken before start of condensation

$$2\ H_3PO_4 \rightarrow H_4P_2O_7 + H_2O$$



Raman Spectroscopy

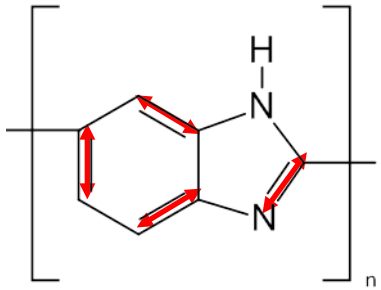
- 5 different doping levels
- 3 spectral regions marked α, β, and γ attributed to benzimidazole ring
- Peak marked with ↑ attributed to free phosphoric acid
- Attribution of the different peaks:
  - o 964 cm^{-1} → ring breathing vibration
  - x 1134, 1176 cm^{-1} → C-C skeletal stretching
  - z 737, 787 cm^{-1} → C-H out-of-plane ring deformation

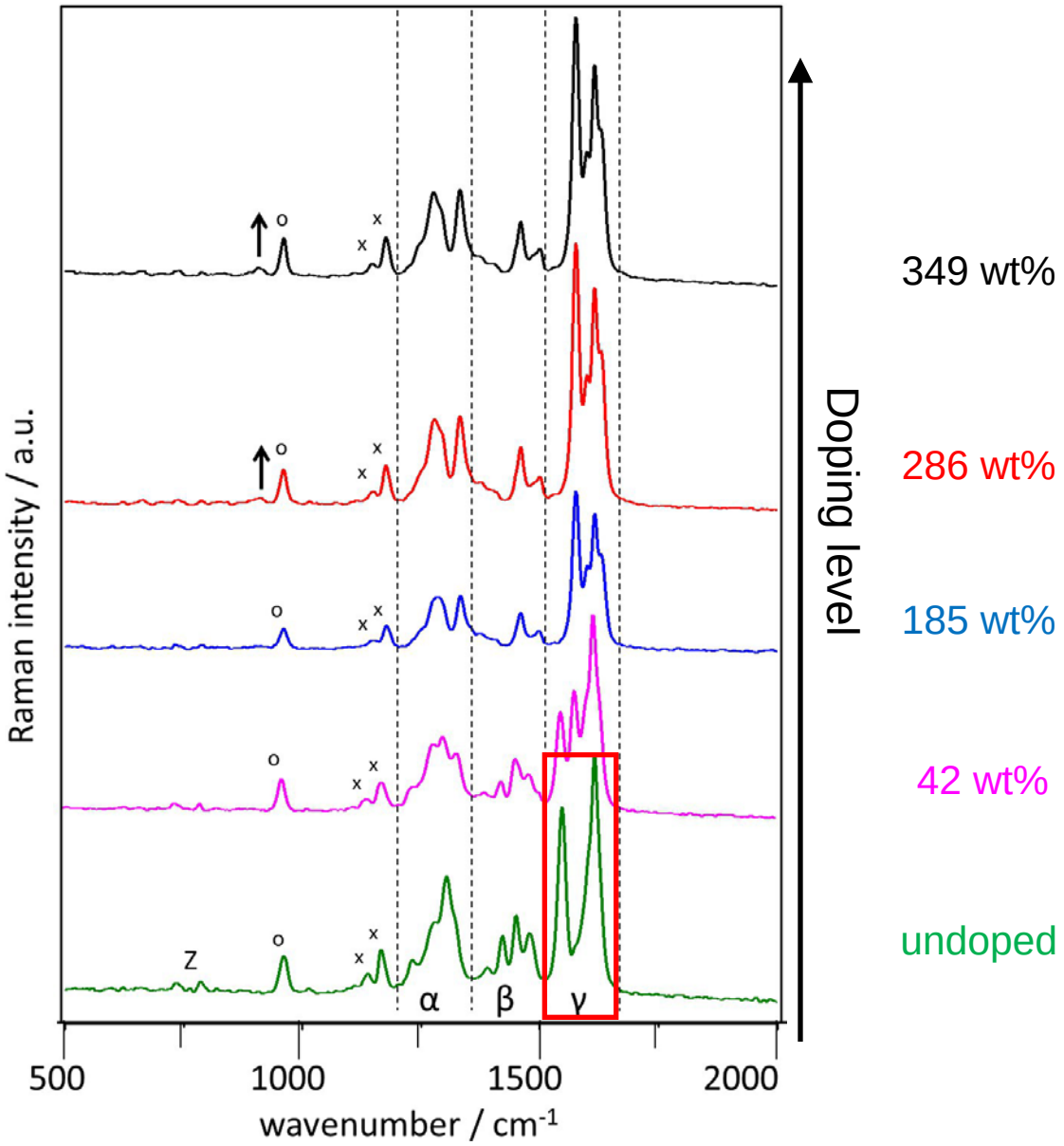


Conti, Majerus, Di Noto, Korte, Lehnert and Stolten
PCCP 14 (2012) 10022-10026

γ region

- 1500 – 1650 cm^{-1}
- Benzimidazole ring
  C=C and C=N vibrations



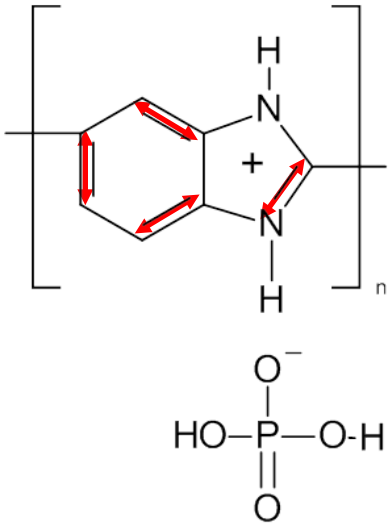


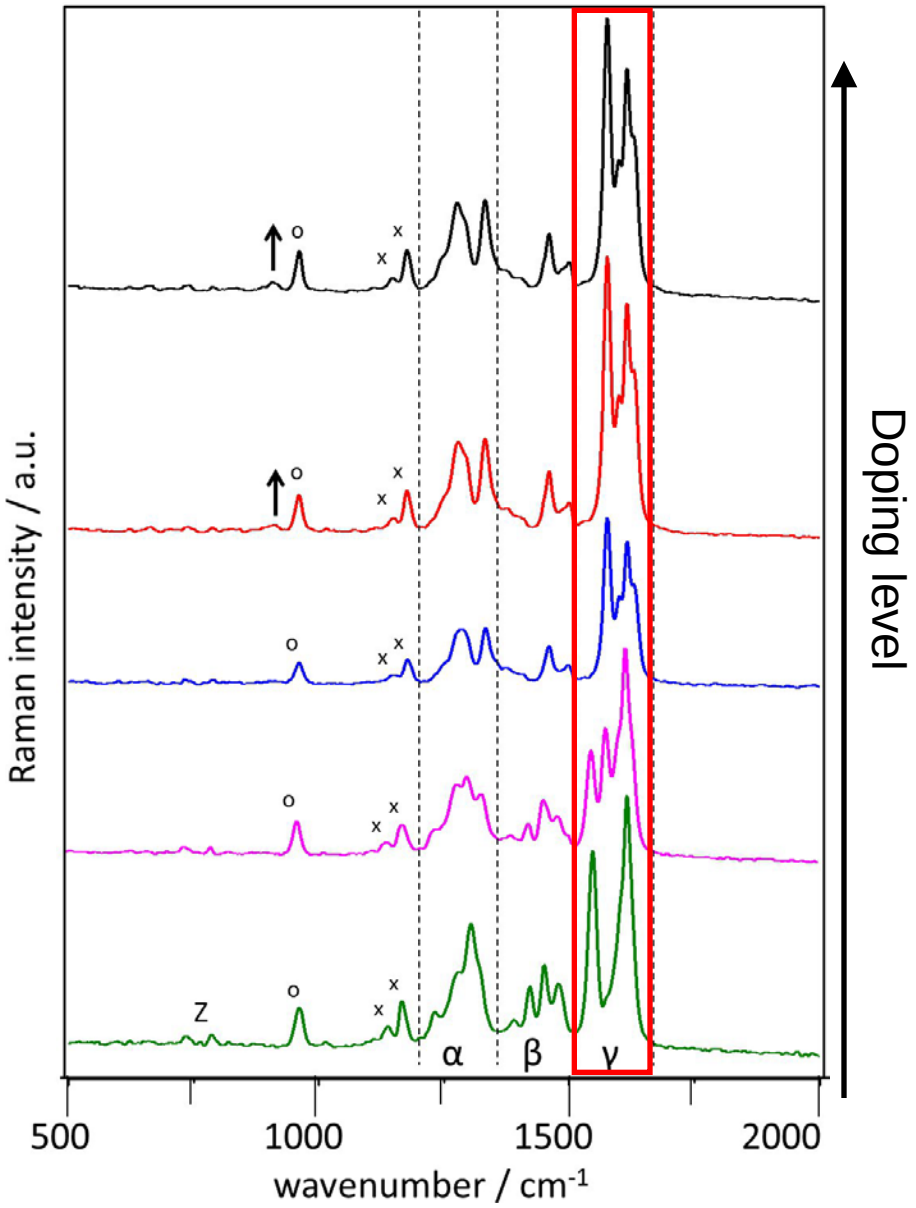
Conti, Majerus, Di Noto, Korte, Lehnert and Stolten
PCCP 14 (2012) 10022-10026

γ region

- 1500 – 1650 cm^{-1}
- Benzimidazole ring
  C=C and C=N vibrations

Formation of hydrogen bonds



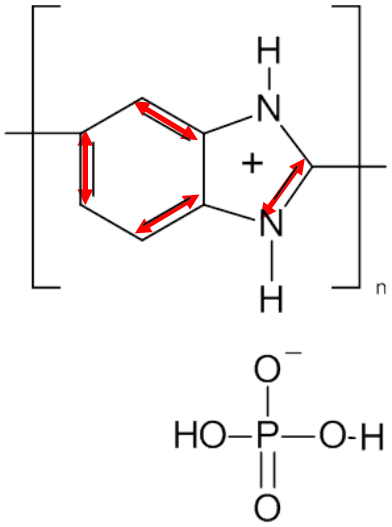


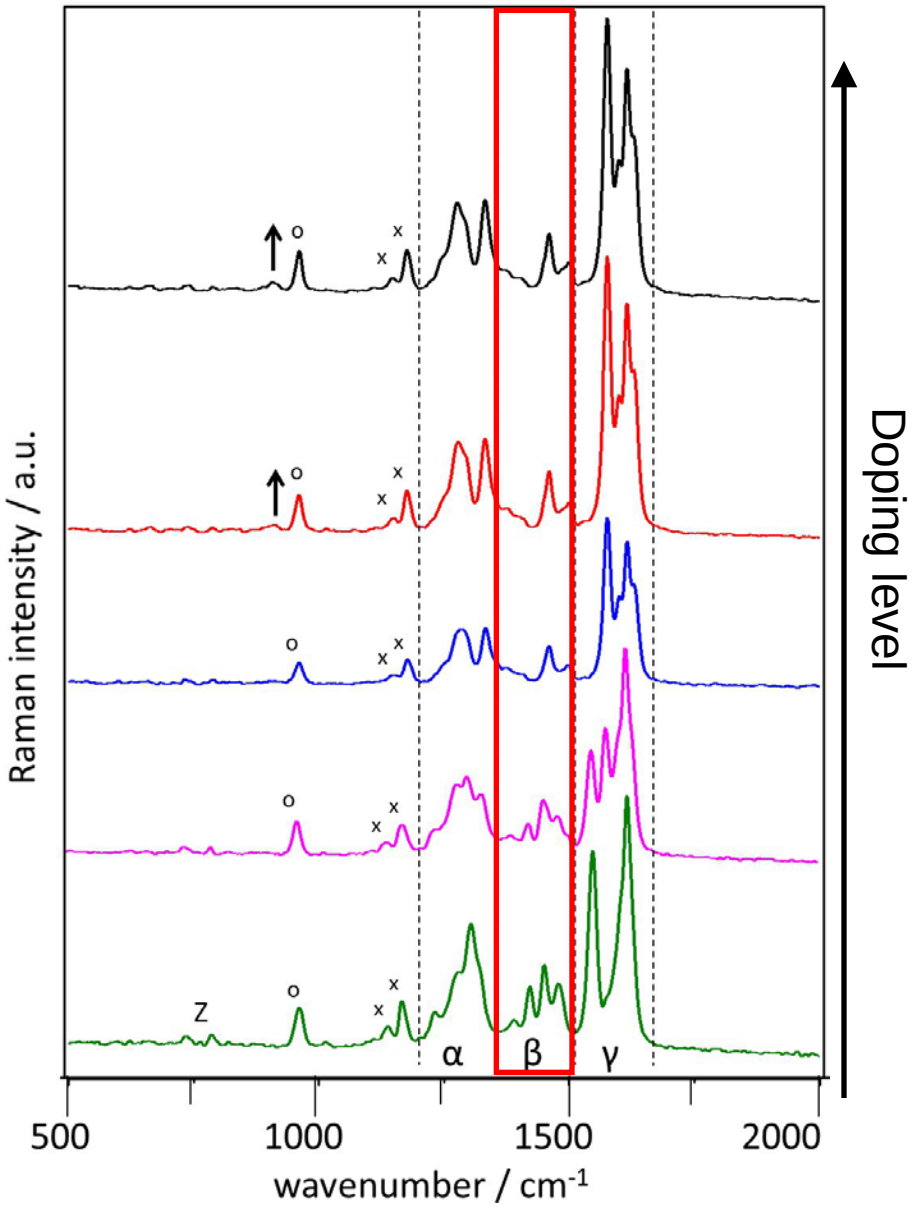
Conti, Majerus, Di Noto, Korte, Lehnert and Stolten
PCCP 14 (2012) 10022-10026

β region

- 1350 – 1500 cm^{-1}
- Benzimidazole ring stretching vibration

Formation of hydrogen bonds



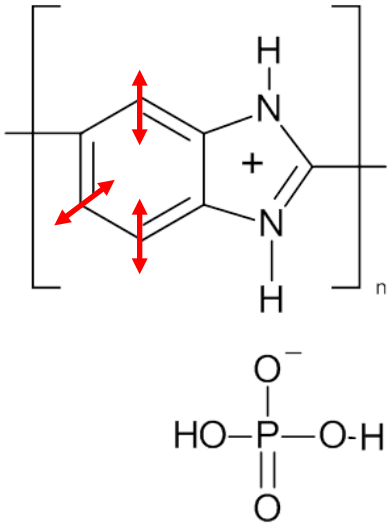


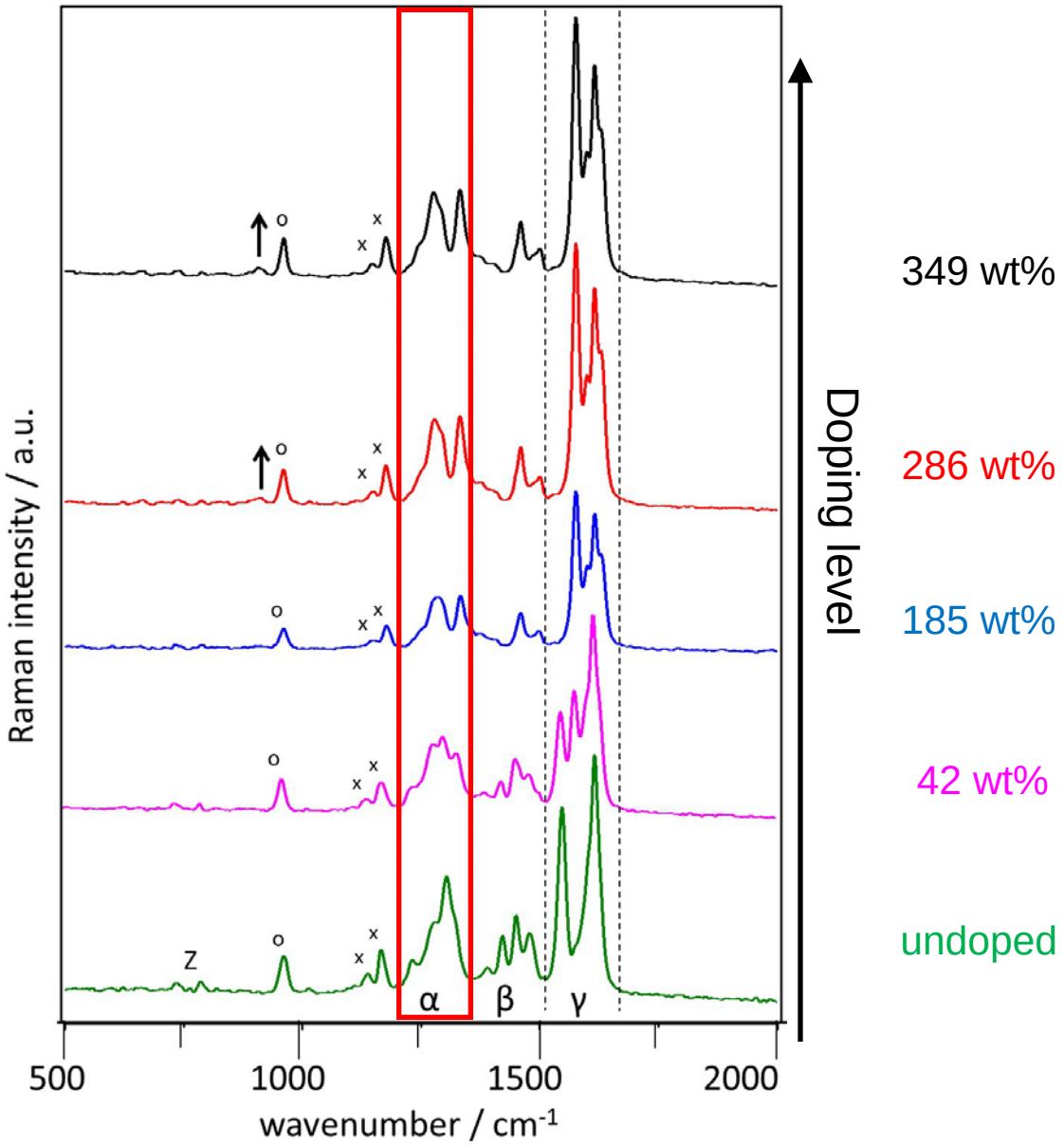
Conti, Majerus, Di Noto, Korte, Lehnert and Stolten
PCCP 14 (2012) 10022-10026

α region

- 1200 – 1350 cm^{-1}
- Benzimidazole ring
  C-H in-plane vibrations

Swelling of the membrane



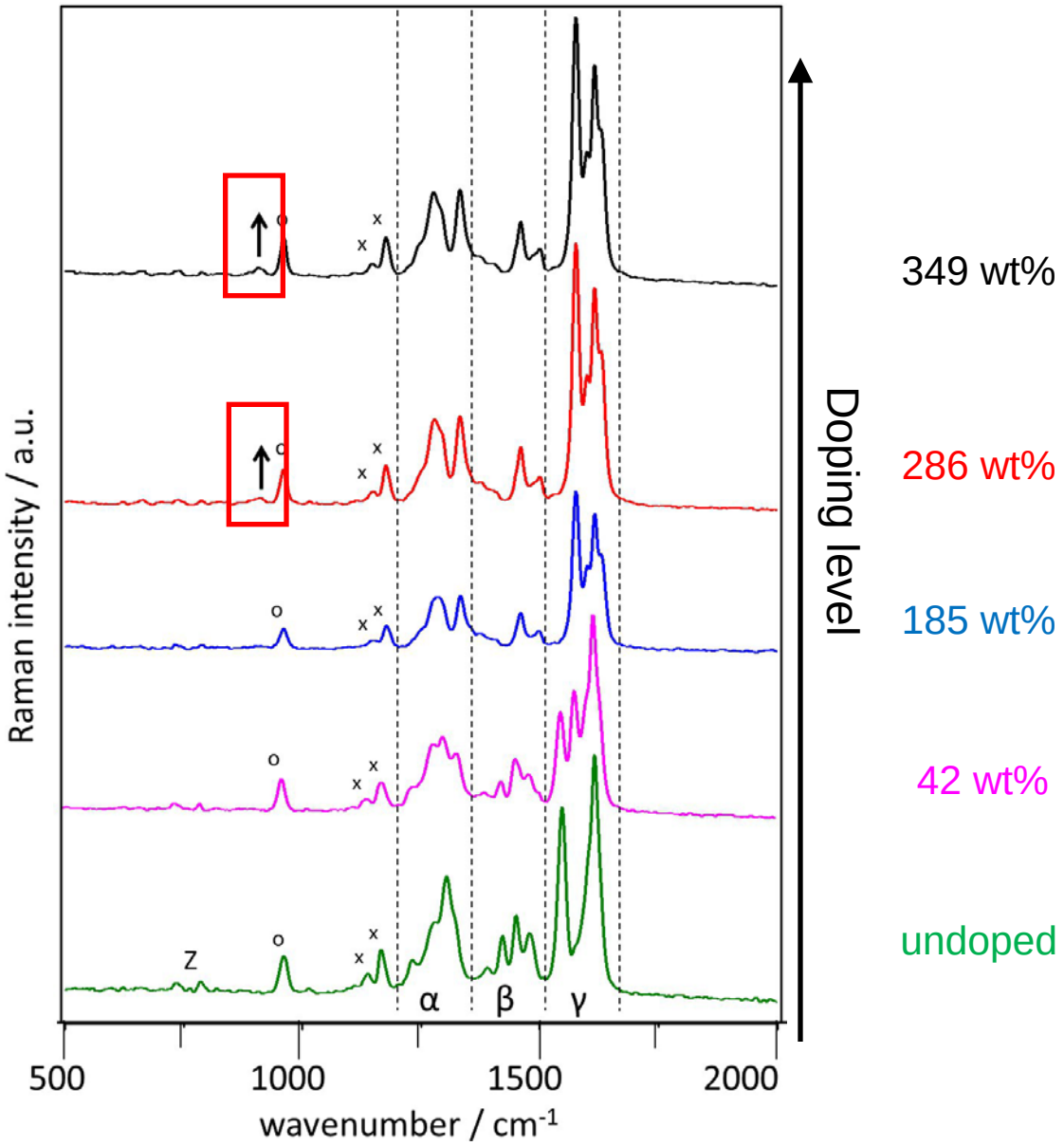


Conti, Majerus, Di Noto, Korte, Lehnert and Stolten
PCCP 14 (2012) 10022-10026

Peak marked with ↑

- 911 cm^{-1}
- Emerges at a doping level of 286 wt% or more
- Same peak visible in the Raman spectrum of pure phosphoric acid

Evidence of free phosphoric acid

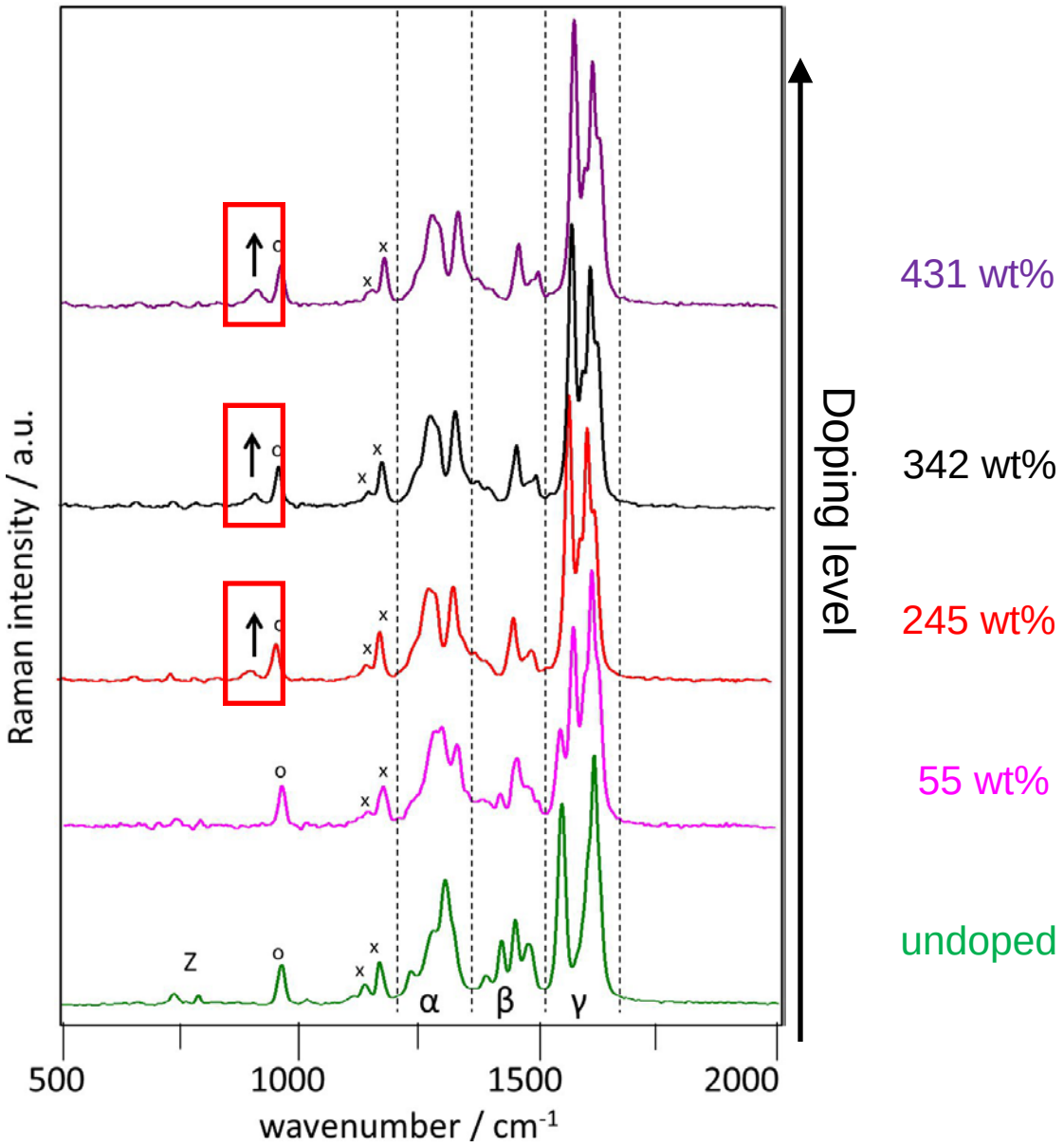


Conti, Majerus, Di Noto, Korte, Lehnert and Stolten
PCCP 14 (2012) 10022-10026

Peak marked with ↑

- 911 cm^{-1}
- Emerges at a doping level of 286 wt% or more
- Same peak visible in the Raman spectrum of pure phosphoric acid

Evidence of free phosphoric acid



Conti, Majerus, Di Noto, Korte, Lehnert and Stolten
PCCP 14 (2012) 10022-10026

Summary

- TGA measurement of phosphoric acid and doped ABPBI
- Plateau in the thermal signal of doped ABPBI
- Phosphoric acid protonates imidazole
- Assumption: bonds need to be broken before start of condensation
- 2 kinds of phosphoric acid: free and bound molecules
- Confirmation by Raman spectroscopy

Thank you for your attention