Politechnika Wrocławska

NEW RESINS DEVELOPMENT: CROSSLINKED ANALOGUES OF IONIC-LIQUIDS

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Background

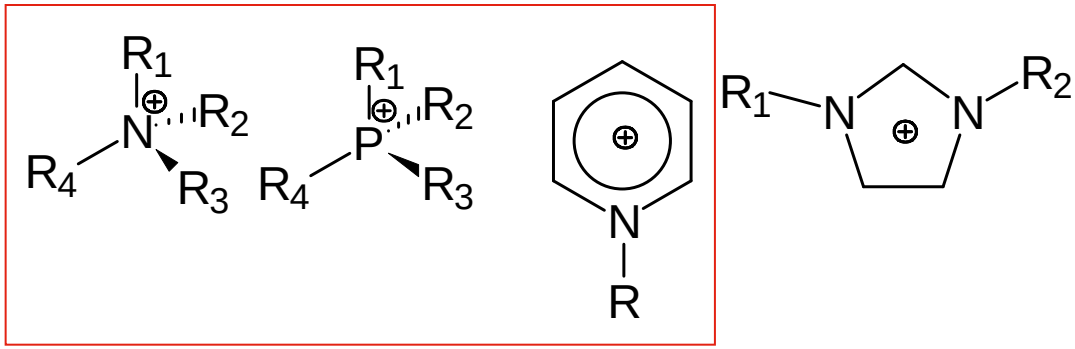
- **Ionic liquids discovered almost 20 years ago:**
- Salts that are liquid at RT (below 80 deg C)
- No vapour pressure
- High polarity
- Composed of ions

- **Possible applications:**
- Media for many reactions
- Extrahents for organic compounds

- **An increase in research on ionic liquids**
- **2006 1259**
- **2005 1015**
- **2004 780**
- **2003 597**
- **2002 417**
- **2001 267**
- **2000 110**
- **1999 66**
- **1998 29**
- **1997 28**
- **1996 21**
- **1995 22**
- **1994 21**
- **1993 22**
- **1992 21**
- **1991 15**
- **1990 3**

Background

- **Typical examples of IL include:**
  - **Ammonium and phosphonium salts**
  - **Pyridinium and dialkylimidazolium**

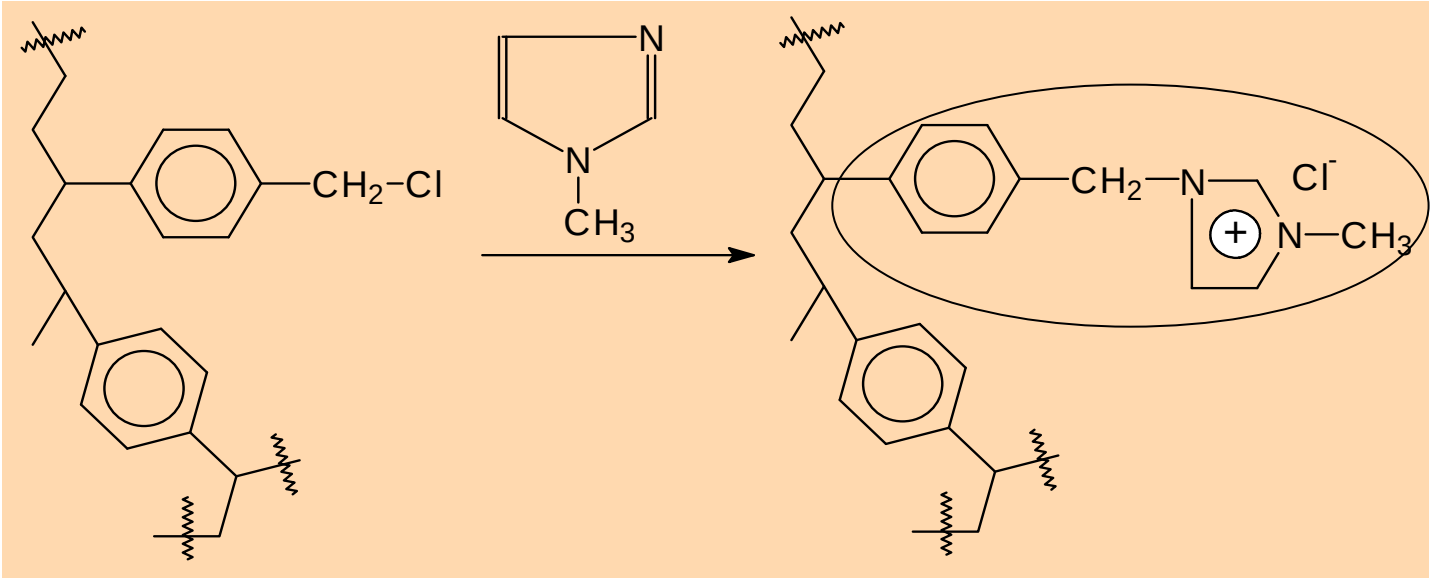


- **CATIONS**
- **ANIONS**
- BF_4^-, PF_6^-, Cl^-, Br^-
- $CF_3SO_3^-$,CF_3COO^-, CH_3COO^-
- $ArSO_3^-$

Synthesis of polymeric resin

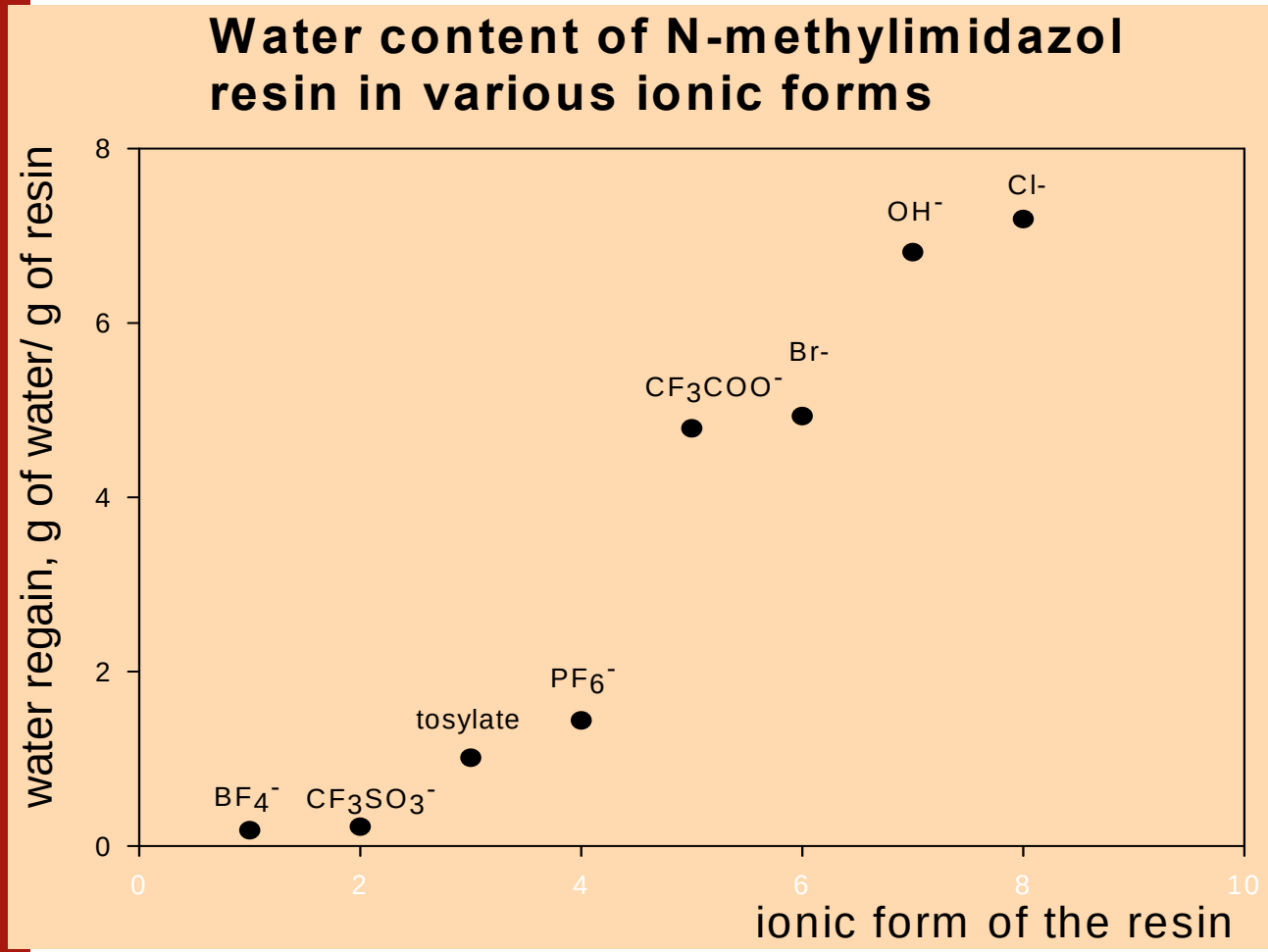
- In some applications it would be advantageous to have insoluble analogues of TSIL in order to avoid problems associated with the separation of such ion-exchange material from the two-phase system and in order to avoid the formation of the third phase and gradual leaching of the extractant.
- In an application to catalysis the recovery of catalyst from the mixture of products, substrates and solvents would be much easier in the case of insoluble analogues TSIL.

Synthesis of polymeric resin



- Good yield of the above reaction
- Thus obtained ion-exchange resin contains ca. 70% by weigth of 'ionic-liquid analogue' (3.5 mmol of ligand/g of polymer)

Water uptake of the polymeric IL analogue



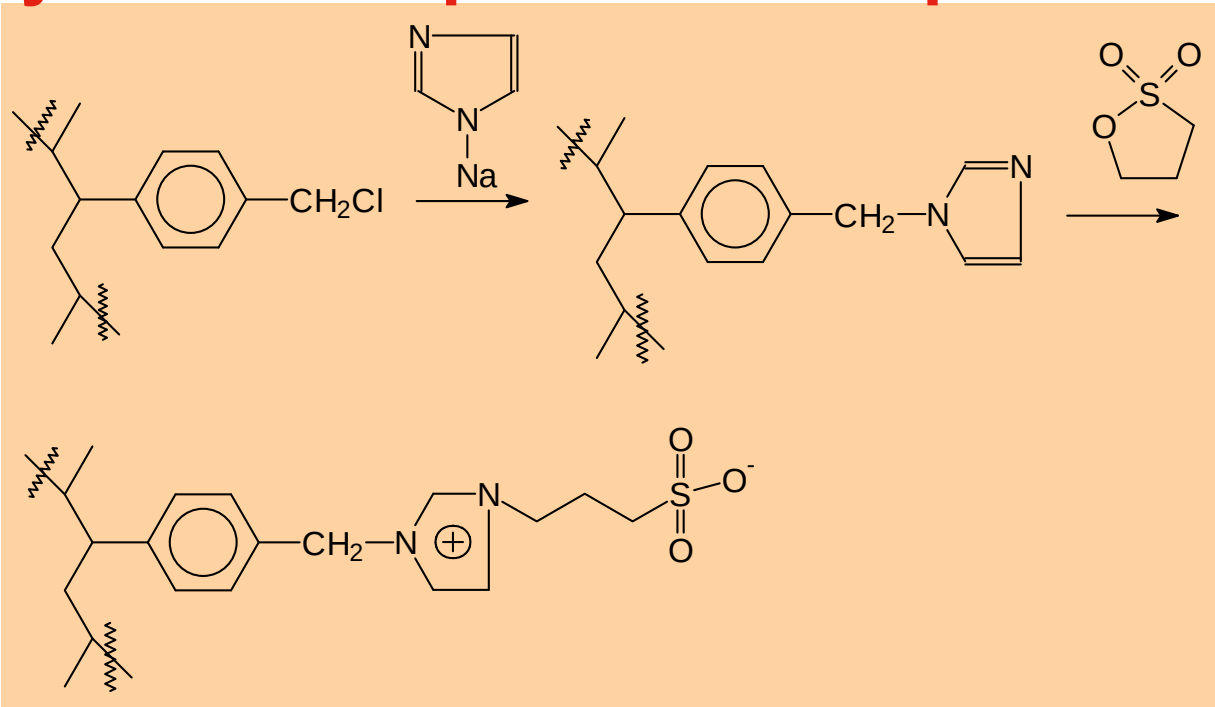
- **Most of us would use it either in chloride or hydroxyl form**

Task-specific IL

- **In last years of XX century a concept of task-specific ionic liquid was developed**
- **They can be defined as IL containing an additional functional group that will perform the task (ion-exchange, coordination, catalytical activity etc.)**

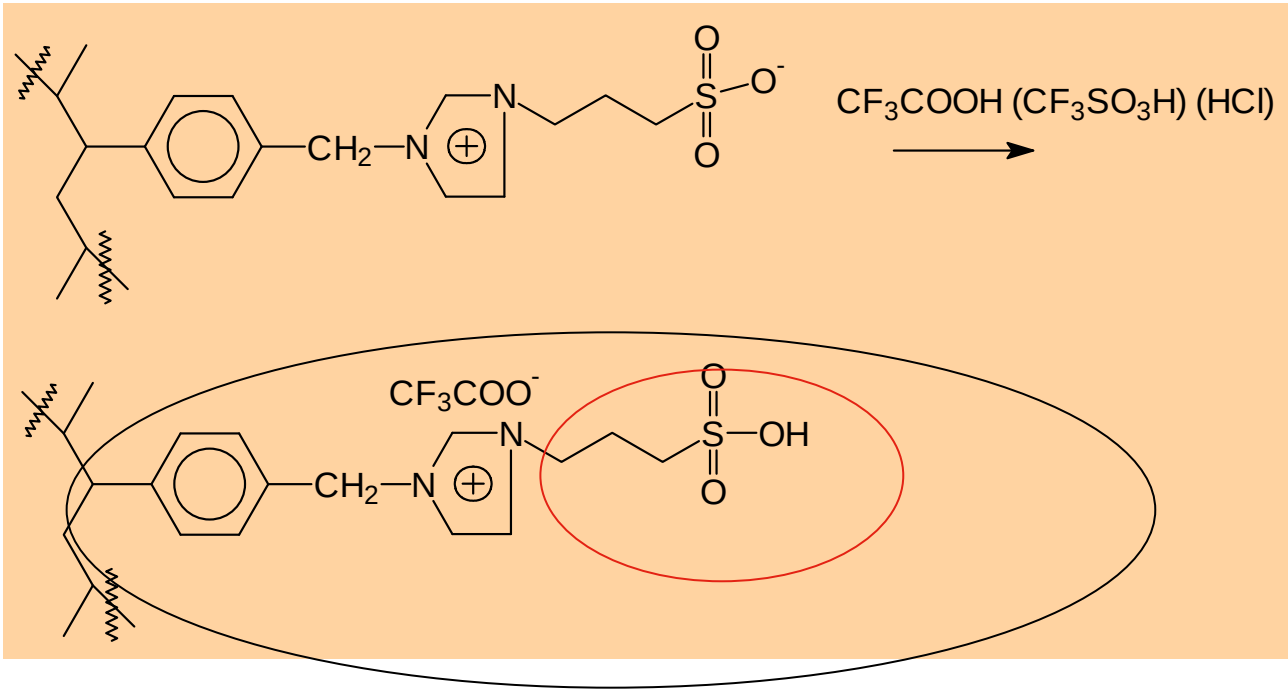
Synthesis of polymeric TSIL analogue

- **Synthesis requires two-step reaction**



- **N content 5,05; S content 3,00; Cl content 0,65 mmol/g**

Ion-exchange of polymeric TSIL analogue



pKa of alkylsulfonic acid is estimated at ca. 2

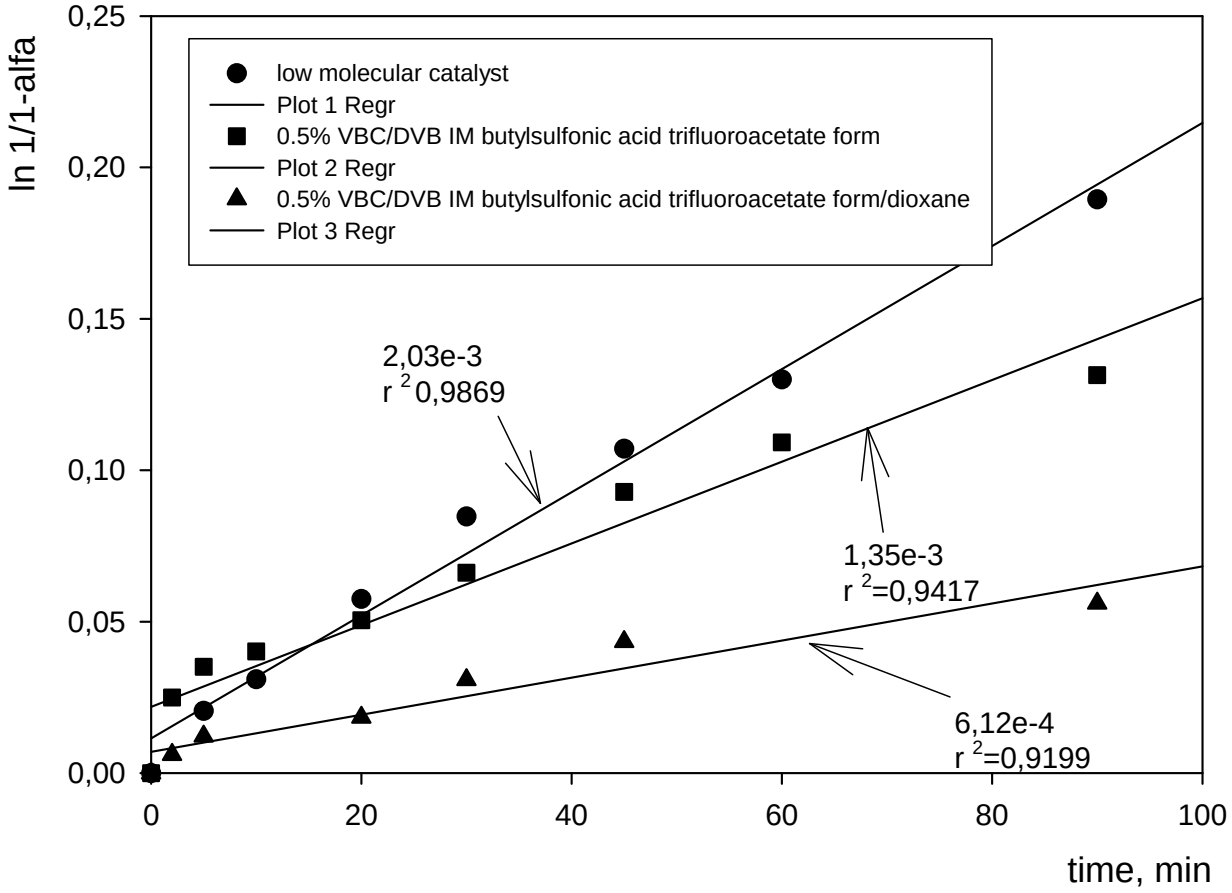
- **Now, because of the size of the attached group, the resin contains up to 80% of TSIL analogue**

Ion-exchange of polymeric TSIL analogue

Anion	Cation	% of solid	Water content g/g
Cl^-	H^+	**46,58**	**1,15**
Br^-	H^+	**56,56**	**0,77**
CF_3COO^-	H^+	**55,55**	**0,80**
$CF_3SO_3^-$	H^+	**70,59**	**0,42**
p-TS$^-$	H^+	**66,20**	**0,51**

Polymeric TSIL analogue as catalysts

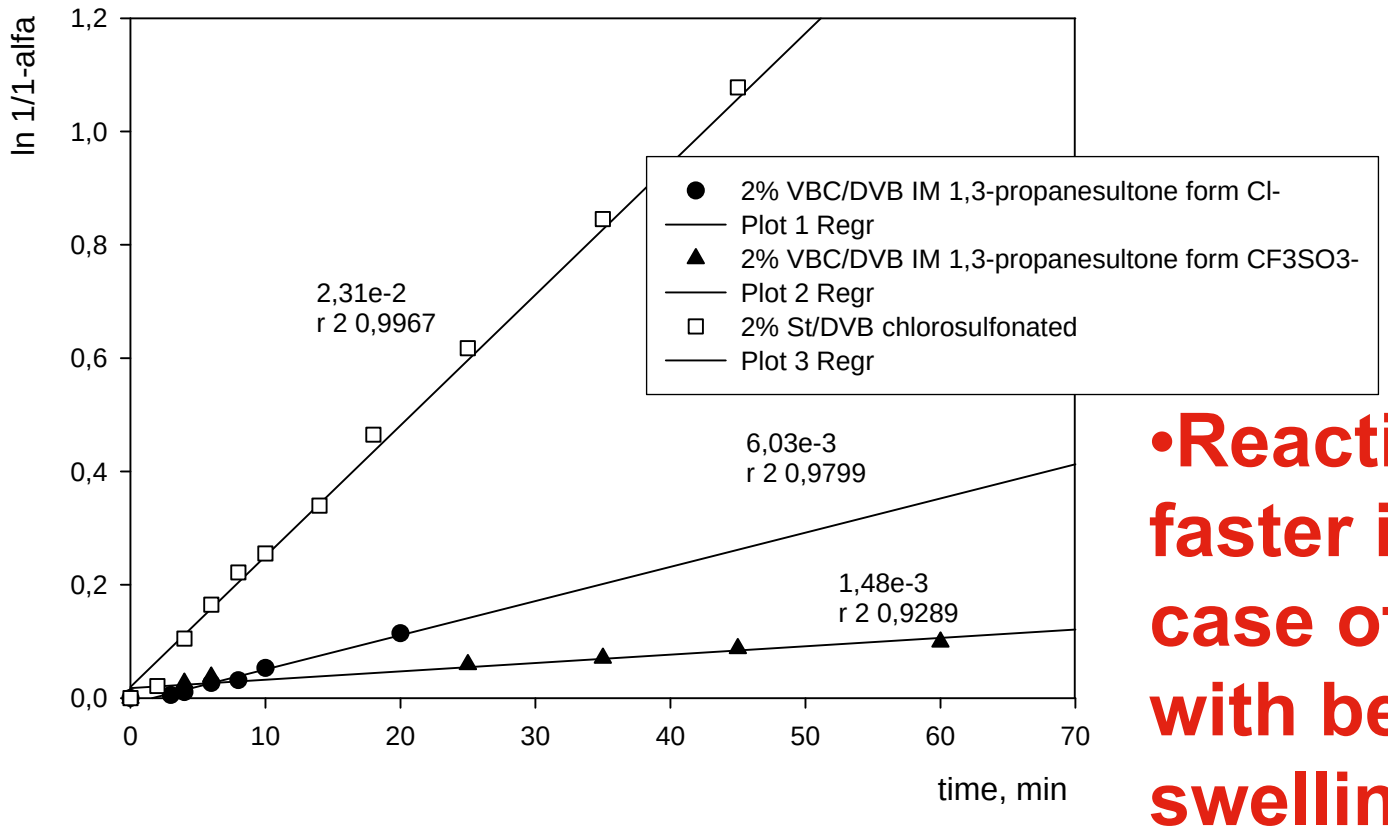
Esterification of acetic acid with butanol



- **Reaction is only one third slower with polymer immobilized TSIL**

Polymeric TSIL analogue as catalysts

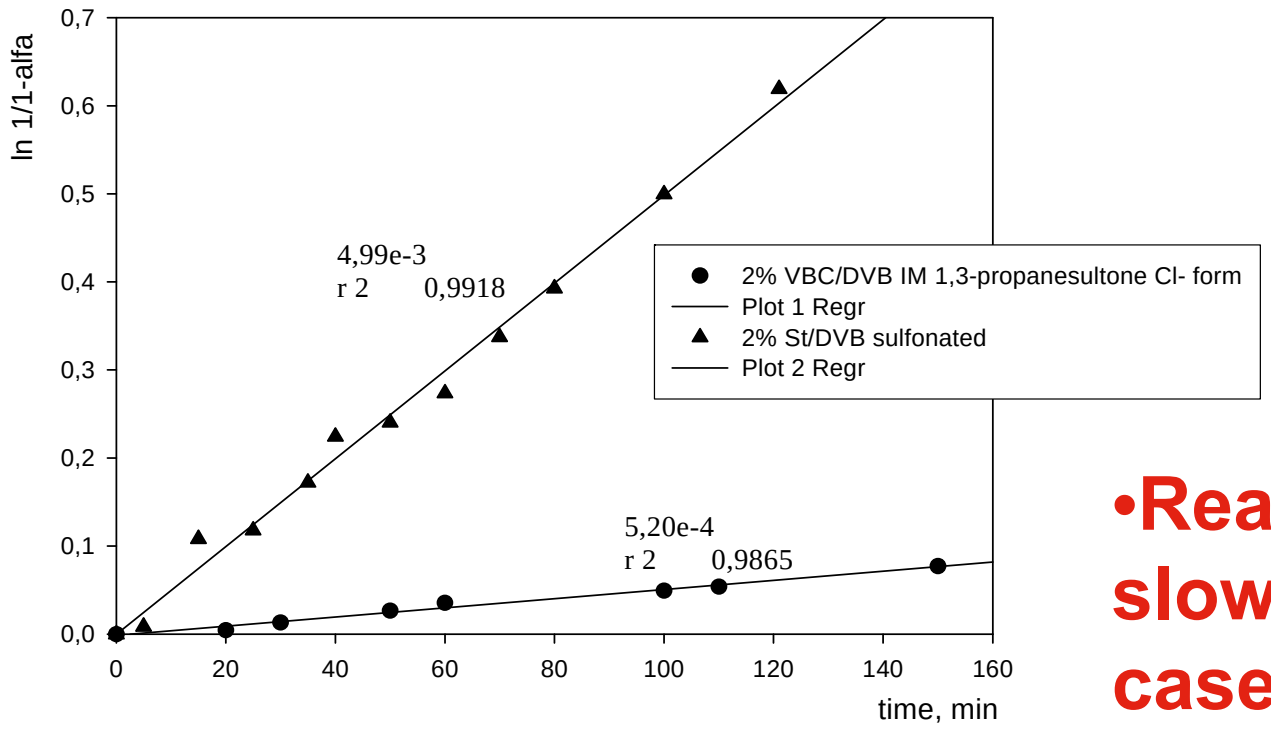
synthesis of butyl acetate



- **Reaction is faster in the case of resin with better swelling**

•Polymeric TSIL analogue as catalysts

octyl hexanoate synthesis



•Reaction is slower in the case of longer acid and alcohol

Conclusions

- It is possible to obtain polymer immobilized Task Specific Ionic Liquid analogues with good yield
- Esterification reaction rate constant are only slightly lower than in the case of low molecular weight TSIL

- ***Thank you for attention***