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Supporting Information for

Polymer Solubility Mechanism in Ionic Liquids: ^{1}H-NMR Spectra and Two-parameter Hydrogen Bonding Analysis

Ming-Xuan Du [1,2], Ya-Fei Yuan[1,2], Jin-Ming Zhang [1], Jia-Jian Liu[1], Chen-Yang Liu[1,2]*

1. CAS Key Laboratory of Engineering Plastics, Beijing National Laboratory for Molecular Sciences, Institute of Chemistry, the Chinese Academy of Sciences, Beijing 100190, China

2. University of Chinese Academy of Sciences, Beijing 10049, China

E-mail:dumingxuan@iccas.ac.cn liucy@iccas.ac.cn

Experimental section

1. Materials

Polymers： Poly(vinyl pyrrolidone) (PVP, M_w = 40000) was purchased from TCI Shanghai Chemical Industry Development Co., Ltd., poly(ethylene oxide) (PEO, M_v = 20000) was purchased from Shanghai Aladdin Bio-technology Co., Ltd, China. Poly(methyl methacrylate) (PMMA, M_n=8000) was synthesized using Reversible Addition-Fragmentation Chain Transfer (RAFT) method. Poly (methyl hydroxyethyl acrylate) (PHEMA) was purchased from Beijing Yinuokai Technology Co., Ltd, China. Poly(vinyl phenol (PVPh, M_w = 11000g/mol) and poly(vinyl alcohol) (PVA, M_w = 30000g/mol) were purchased from Sigma Aldrich.

Ionic Liquids: 1-Butyl-3-methylimidazolium bis((trifluoromethane)sulfonyl)imide ([C_4mim][NTf_2], 99%) and 1-Butyl-3-methylimidazolium acetate ([C_4mim][Ac], 99%) were purchased form Center for Green Chemistry and Catalysis of Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences.

2. ^{1}H-NMR spectrum measurement

All the ^{1}H-NMR measurement were tested on a Bruker AV 400 spectrometer with 16-64 scans at 298K, using TMS as an internal reference. For β-Type polymers/[C_4mim][NTf_2], CD_2Cl_2 is adopt as deuterium reagent. [C_4mim][NTf_2]:CD_2Cl_2 is fixed at 1:500 and [C_4mim][NTf_2]: β-Type polymers are 1:1, 1:5, 1:10, 1:20, 1:35, 1:50 and 1:100 respectively. For α-Type polymers/[C_4mim][Ac], DMSO-d_6 is used as deuterium reagent. [C_4mim][Ac]:DMSO-d_6 is fixed at 1:14 and [C_4mim][Ac]: α-Type polymers are 1:0.15, 1:0.3, 1:0.75, 1:1 and 1:3 respectively.

3. Solubility experiment of PVPh in ILs

The solubility experiments of PVPh in ILs followed the methods reported in the literature[1]. Due to the high viscosity of ILs, the dissolution of PVPh (3 wt%) was carried out at 80 °C for 10 h. Then cool to room temperature and let stand for 72 h. PVPh was regarded as soluble in ILs when the PVPh/ILs solutions were

homogeneous and transparent, otherwise, PVPh was regarded as insoluble in ILs.

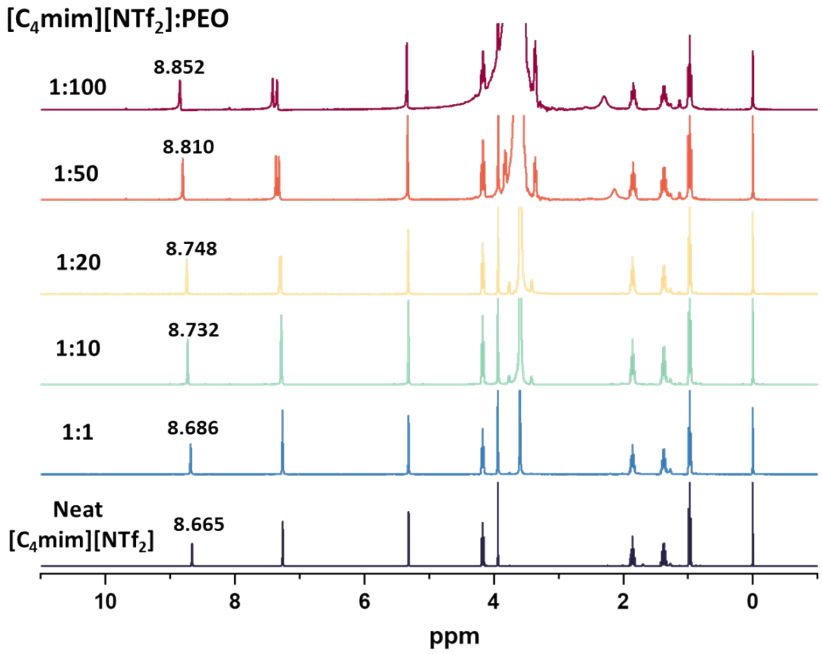

Figure S1. The ^{1}H-NMR spectra of [C_4mim][Ntf_2]/PEO in CD_2Cl_2.

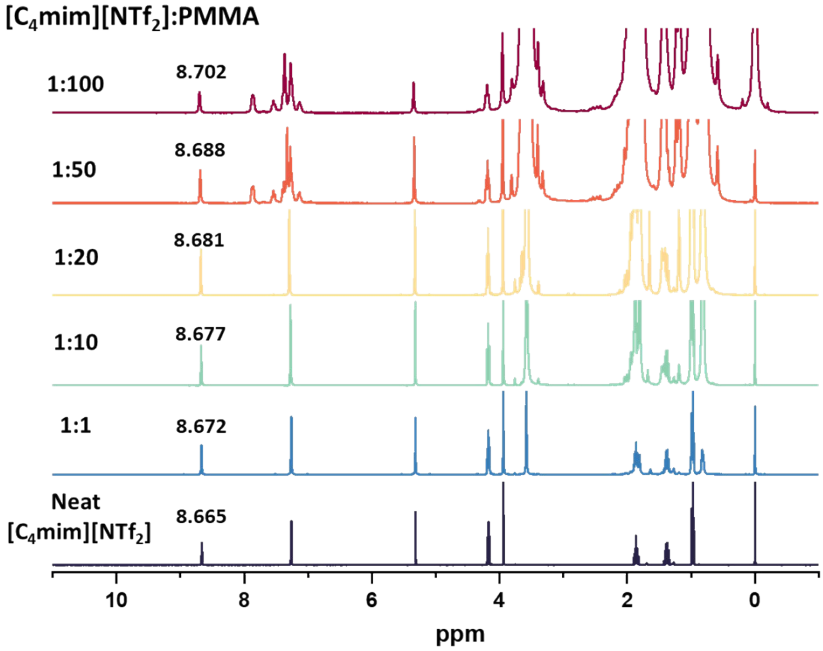

Figure S2. The ^{1}H-NMR spectra of [C_4mim][Ntf_2]/PMMA in CD_2Cl_2.

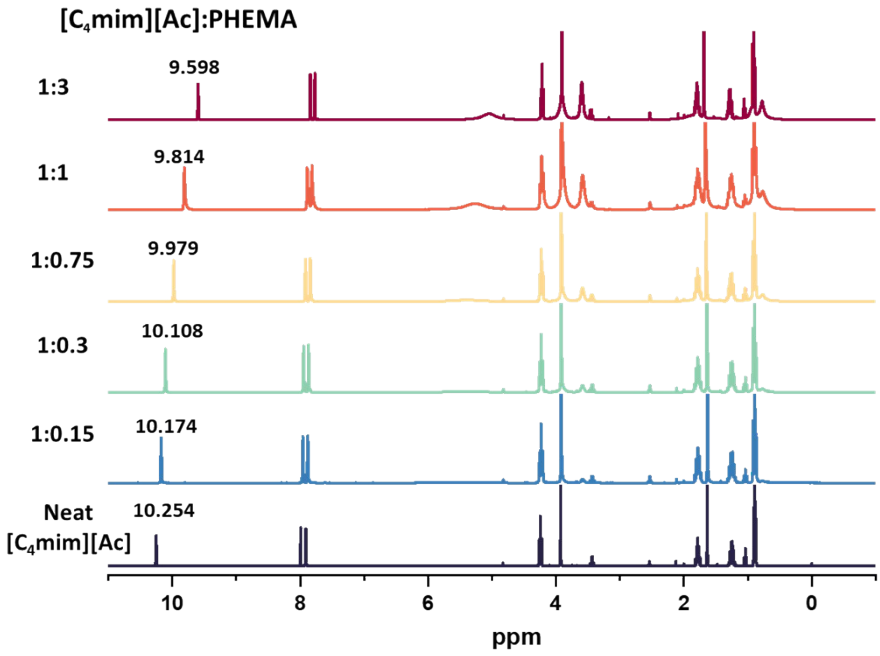

Figure S3. The ^{1}H-NMR spectra of [C_4mim][Ac]/PHEMA in DMSO-d_6.

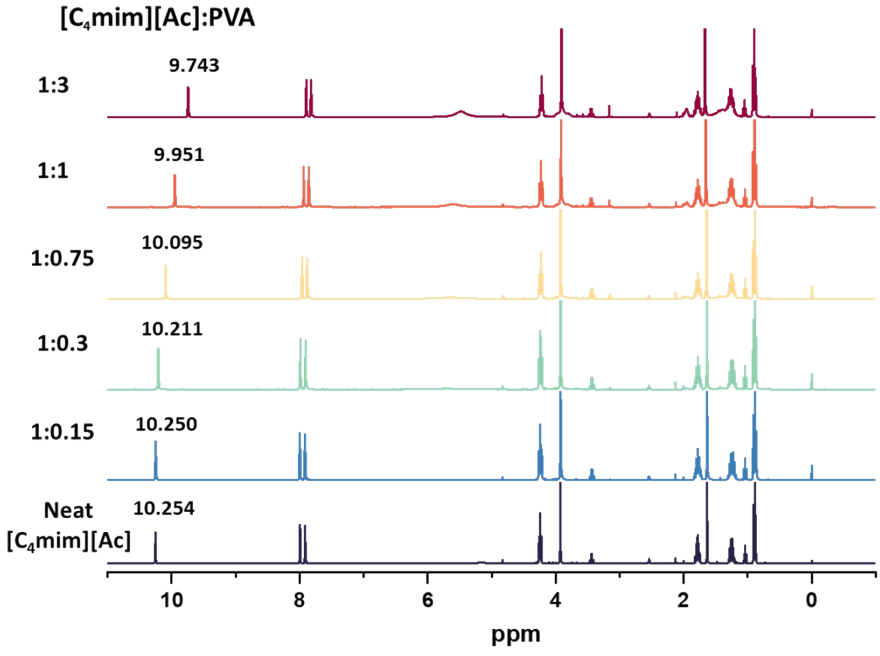

Figure S4. The ^{1}H-NMR spectra of [C_4mim][Ac]/PVA in DMSO-d_6.

Table S1. Solubility results of PVPh in ILs. (KT parameters of ILs cited from Ref 2)

Ionic liquids	α	β	Solubility
$[C_2mim][Ac]$	0.57	1.06	soluble
$[C_4mim][Ac]$	0.43	1.05	soluble
$[C_4mim][MeSO_3]$	0.53	0.66	soluble
$[C_4mim][TFO]$	0.62	0.49	soluble
$[C_2mim][BF_4]$	-	-	soluble
$[C_4mim][BF_4]$	0.63	0.37	soluble
$[C_4mim][N(CN)_2]$	0.54	0.60	soluble
$[C_2mim][NTf_2]$	0.71	0.23	insoluble
$[C_4mim][NTf_2]$	0.72	0.24	insoluble
$[C_8mim][NTf_2]$	0.60	0.29	insoluble
$[C_4mim][PF_6]$	0.63	0.19	insoluble
$[C_6mim][PF_6]$	-	-	insoluble
$[C_8mim][PF_6]$	-	-	insoluble

Reference

1 Y. F. Yuan, J. M. Zhang, B. Q. Zhang, J. J. Liu, Y. Zhou, M. X. Du, L. X. Han, K. J. Xu, X. Qiao and C. Y. Liu, Polymer solubility in ionic liquids: dominated by hydrogen bonding. *Phys. Chem. Chem. Phys.*, 2021, **23**, 21893−21900.

2 M. A. Ab Rani, A. Brant, L. Crowhurst, A. Dolan, M. Lui, N. H. Hassan, J. P. Hallett, P. A. Hunt, H. Niedermeyer, J. M. Perez-Arlandis, M. Schrems, T. Welton and R. Wilding, Understanding the polarity of ionic liquids, *Phys. Chem. Chem. Phys.*, 2011, **13**, 16831–16840.