Improved Thermal Stability of Imidazolium Treatments for Polymer Layered-Silicate Nanocomposites

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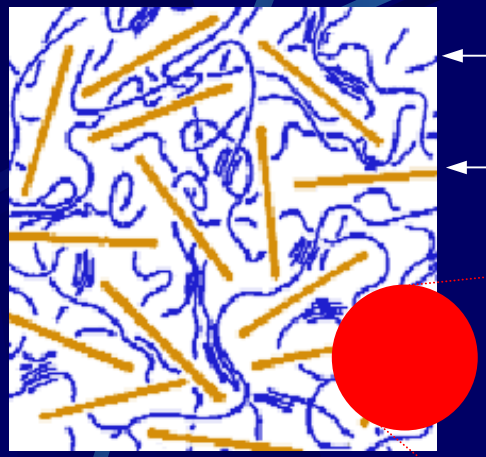
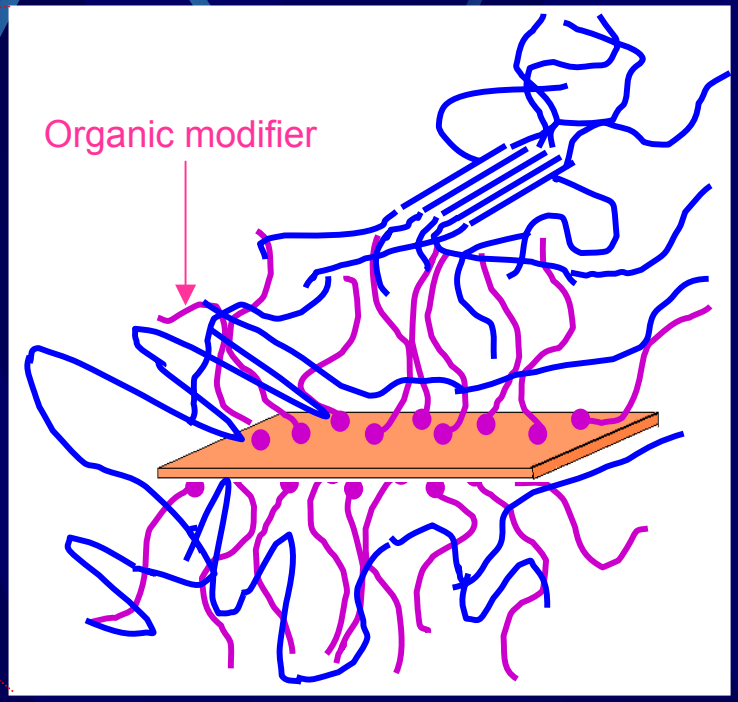
BUILDING AND FIRE RESEARCH LABORATORY

Polymer Layered-Silicate Nanocomposites



Polymer

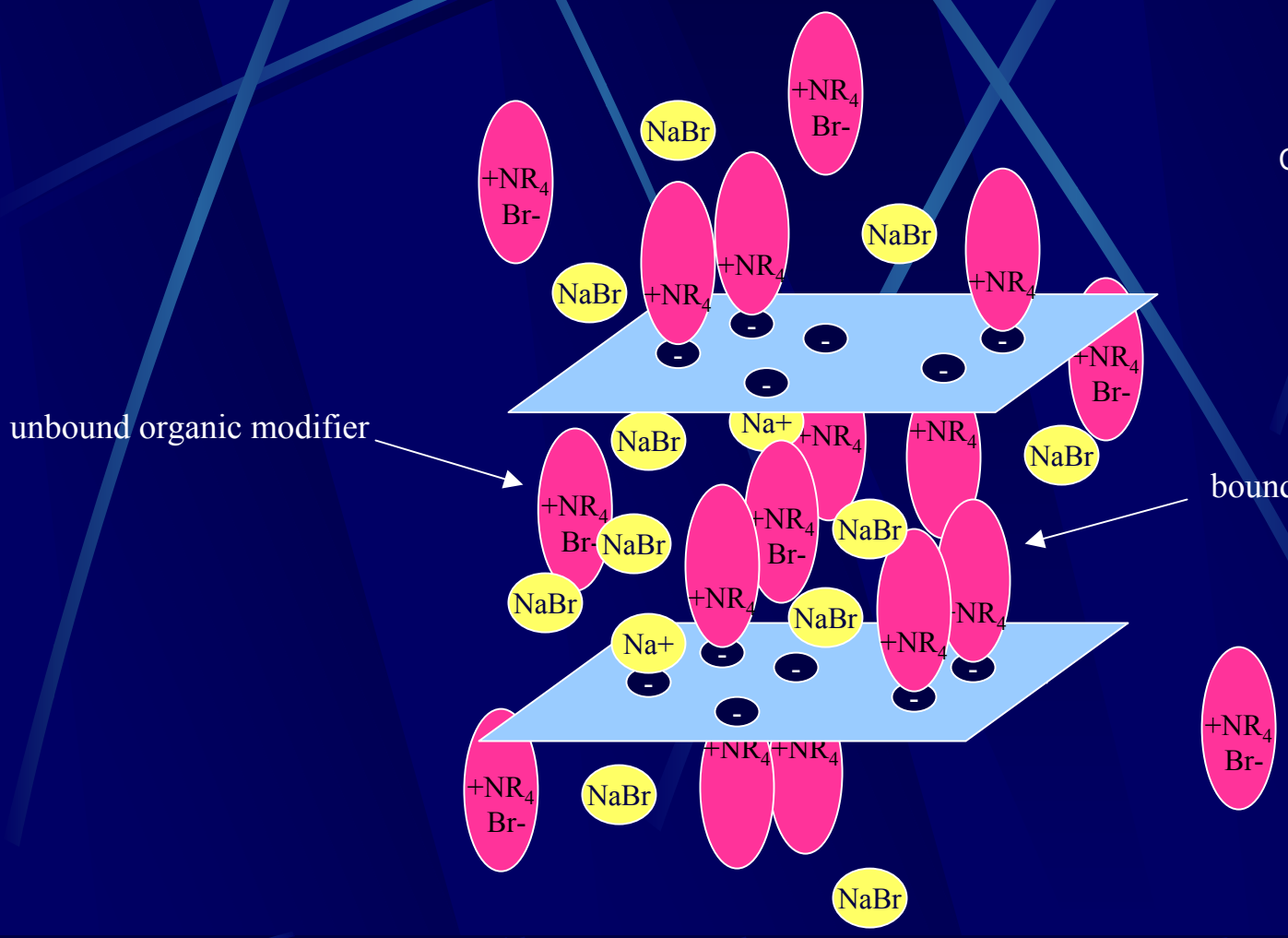
Organically treated clay sheets (50 nm x 50 nm x 1 nm)

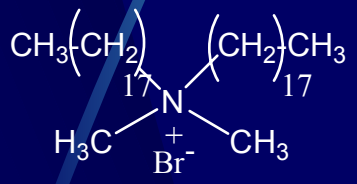


Advantages:
- decreased flammability
- increased properties
- inexpensive

Problems with degradation
- limited recycling – toxic
- decreased mechanical properties
- increased flammability
- limited commercialization

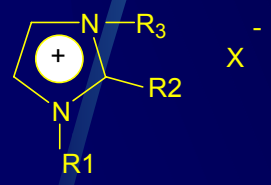
Organic Modification of Clay





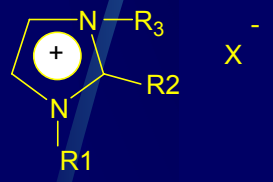
Alkyl-Imidazolium Salt Synthesis

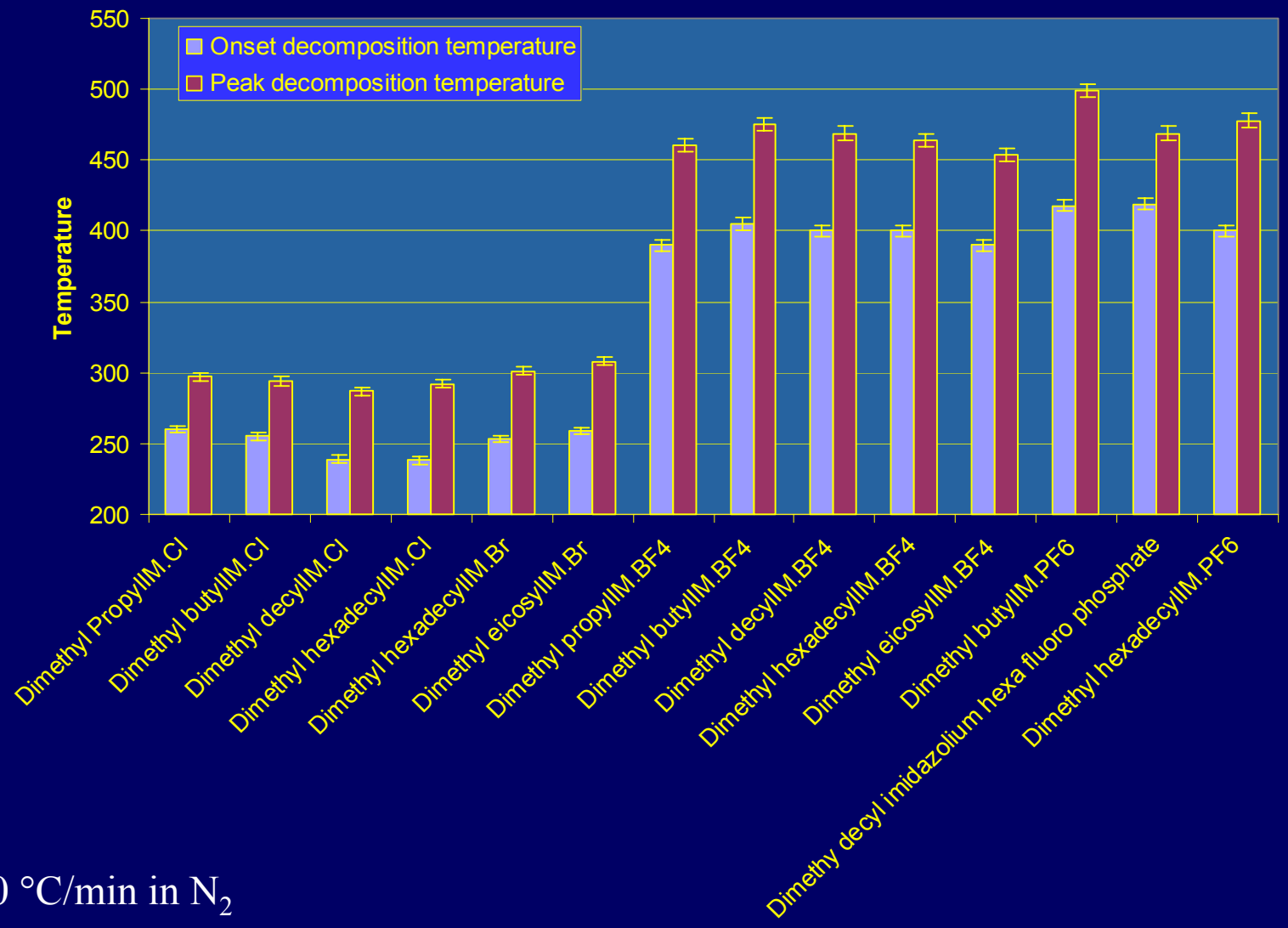
Alkyl-Imidazolium Molten Salts



Salt	R1	R2	R3	X^-
DMPIM.Cl	Methyl	Methyl	Propyl	Cl^-
DMBIM.Cl	Methyl	Methyl	Butyl	Cl^-
DMHDIM.Cl	Methyl	Methyl	Hexadecyl	Cl^-
DMDIM.Cl	Methyl	Methyl	Decyl	Cl^-
MHBIM.Cl	Methyl	H	Butyl	Cl^-
MHHDIM.Cl	Methyl	H	Hexadecyl	Cl^-
DMEtIM.Br	Methyl	Methyl	Ethyl	Br^-
DMHDIM.Br	Methyl	Methyl	Hexadecyl	Br^-
DMEiIM.Br	Methyl	Methyl	Eicosyl	Br^-
MHEtBIM.Br	Methyl	Methyl	Ethyl benzene	Br^-
DOIM.BF_4	Octadecyl	H	Octadecyl	BF_4^-
DMPIM.BF_4	Methyl	Methyl	Propyl	BF_4^-
DMBIM.BF_4	Methyl	Methyl	Butyl	BF_4^-
DMiBIM.BF_4	Methyl	Methyl	Isobutyl	BF_4^-
DMDIM.BF_4	Methyl	Methyl	Decyl	BF_4^-
DMHDIM.BF_4	Methyl	Methyl	Hexadecyl	BF_4^-
DMAlIM.BF_4	Methyl	Methyl	Allyl	BF_4^-
DMEiIM.BF_4	Methyl	Methyl	Eicosyl	BF_4^-
DMiBIM.PF_6	Methyl	Methyl	Isobutyl	PF_6^-
DMBIM.PF_6	Methyl	Methyl	Butyl	PF_6^-
DMDIM.PF_6	Methyl	Methyl	Decyl	PF_6^-
DMHDIM.PF_6	Methyl	Methyl	Hexadecyl	PF_6^-
DMEtBIM.PF_6	Methyl	Methyl	Ethyl benzene	PF_6^-
DMMeOEtOEtIM.PF_6	Methyl	Methyl	Methoxy ethoxy ethyl	PF_6^-
MHEtIM.$N(SO_2CF_3)_2$	Methyl	H	Ethyl	$N(SO_2CF_3)_2^-$

Alkyl-Imidazolium Thermal Stability: Effect of Anion Type

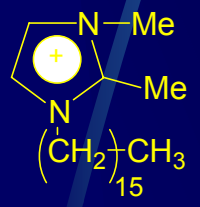




10 °C/min in N_2

Alkyl-Imidazolium Decomposition Temperatures

R_2=H, Me



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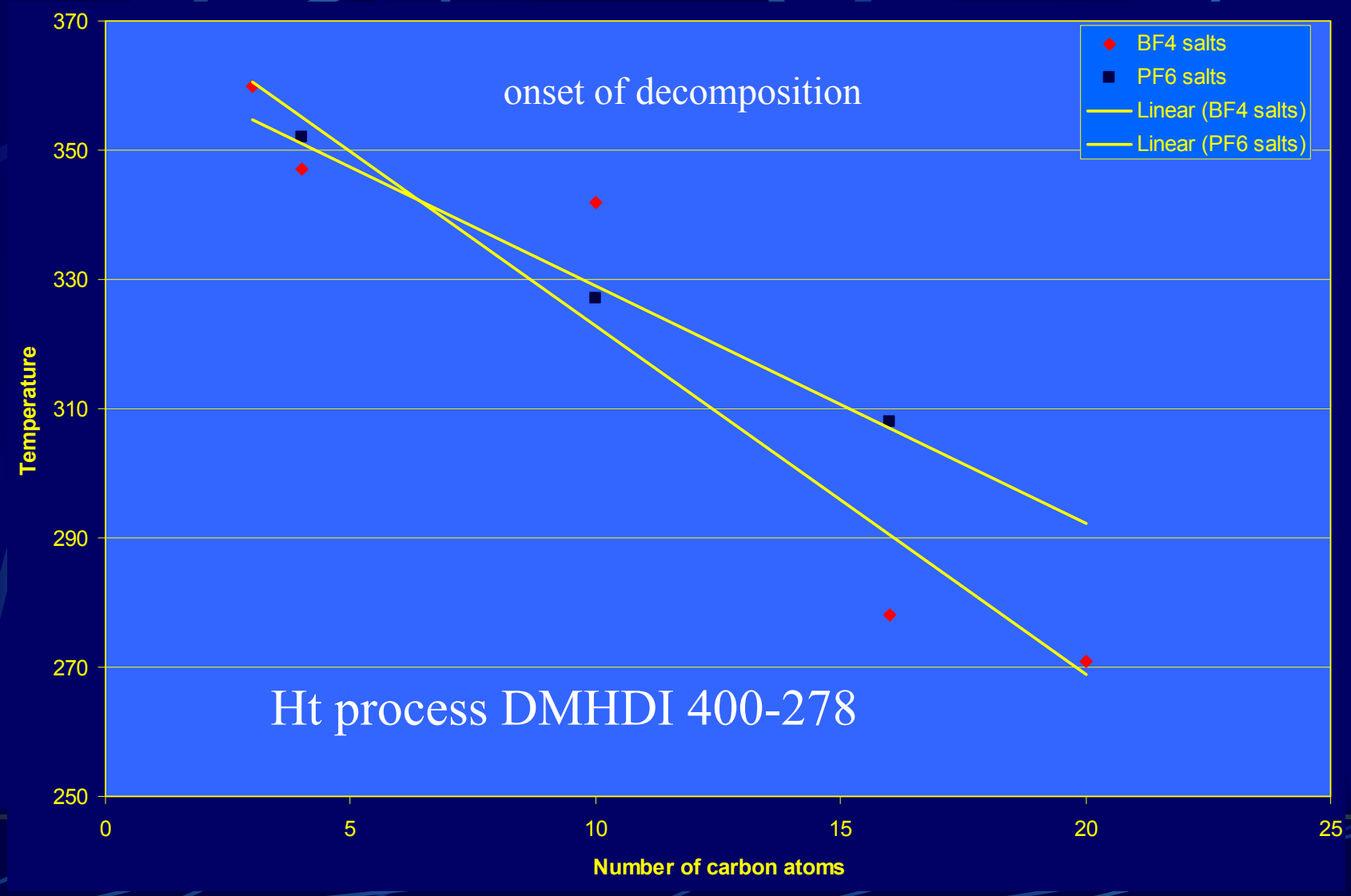
Clay

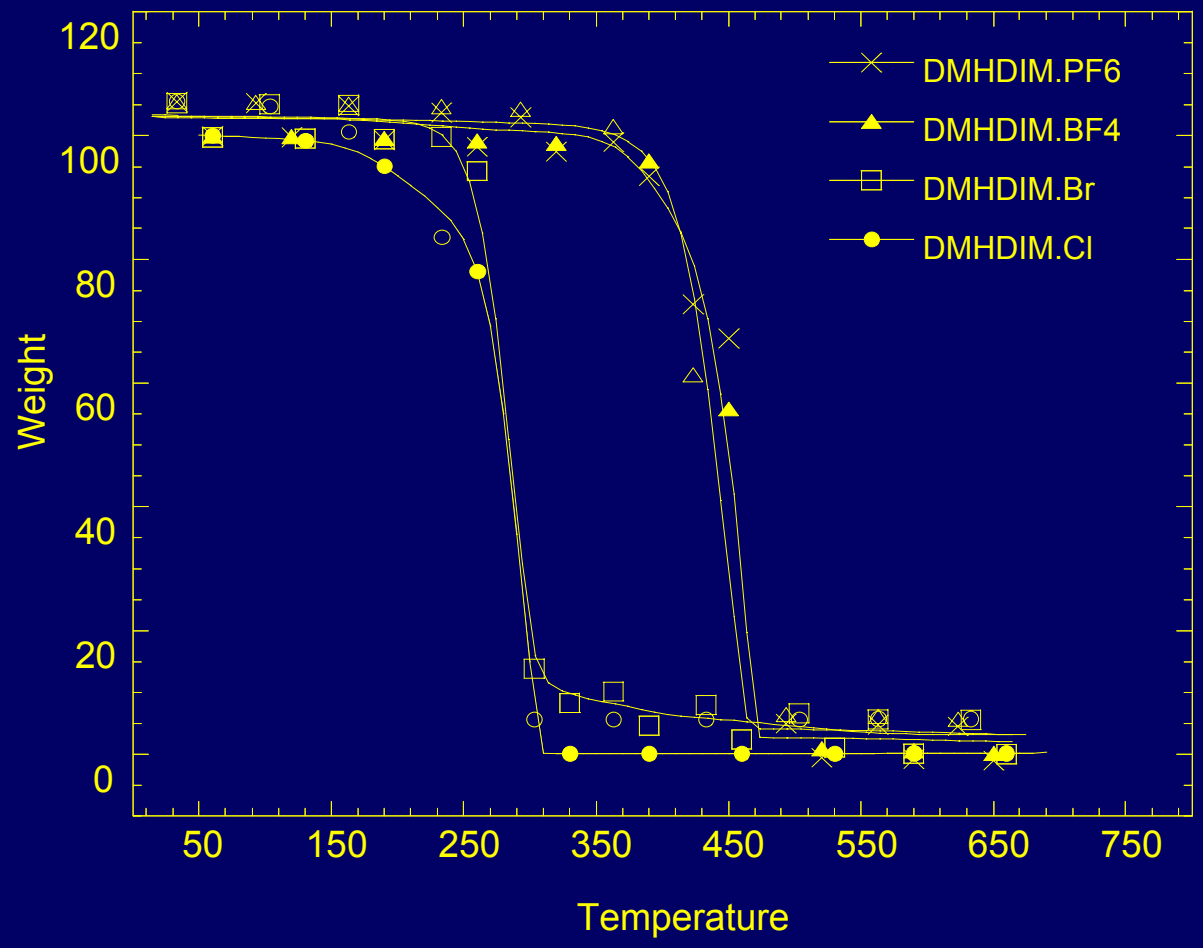
Sample	TGA, °C (under N_2)		TGA, °C (under air)	
	T_{onset}	T_{peak}	T_{onset}	T_{peak}
DMDODA.Br	225	236	185	228
DMPIM.Cl	260	297	259	299
DMBIM.Cl	257	294	255	294
MHBIM.Cl	234	285	232	284
DMDIM.Cl	239	287	237	284
MHHDIM.Cl	230	292	229	287
DMHDIM.Cl	239	292	239	286
DMHDIM.Br	253	301	250	304
DMEiIM.Br	259	308	260	315
DMEtBIM.Br	275	339		
DODMIM.Br	240	314		
DMPIM.BF_4	390	461	360	434
DMBIM.BF_4	405	475	347	428
DMiBIM.BF_4	350	429	347	404
DMDIM.BF_4	400	469	342	425
DMHDIM.BF_4	400	464	278	391
DMAlIM.BF_4	332	410		
DMEiIM.BF_4	390	454	271	406
DMBIM.PF_6	425	499	358	396
DMBIM.PF_6	382	439	357	424
DMDIM.PF_6	420	469	327	376
DMHDIM.PF_6	400	478	308	370
DMEtBIM.PF_6	386	464	334	397
DMMeOEtOIM.PF_6	360	408	300	374
MHEtIM($N(SO_2CF_3)_2$)	410	479	401	477

Uncertainity ± 1.2 °C (2 sigma)

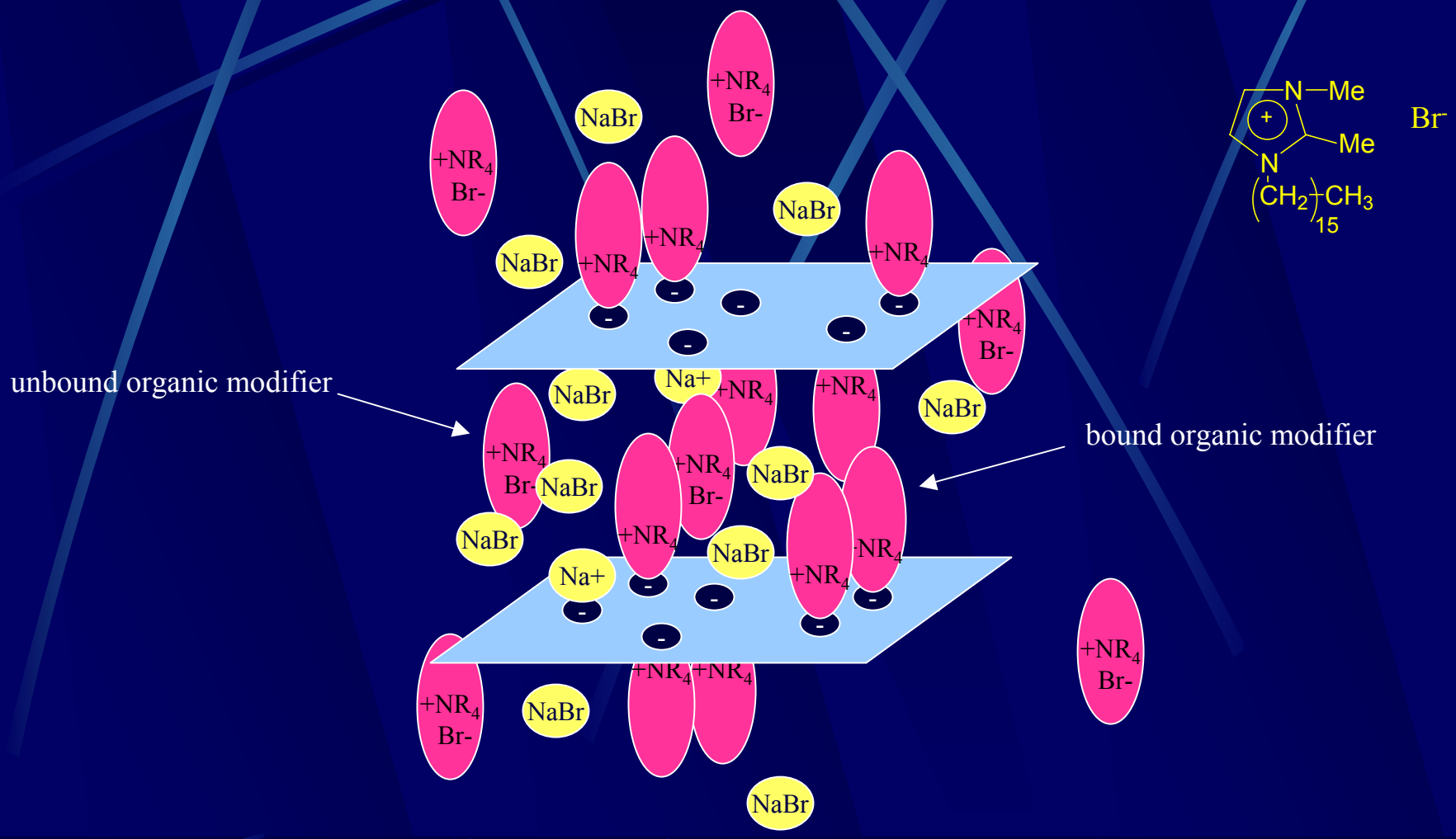
Alkyl-Imidazolium Oxidative Decomposition: Effect of Chain Length



Alkyl-Imidazolium Thermal Stability: Effect of Anion Type



Organic Modification of Clay



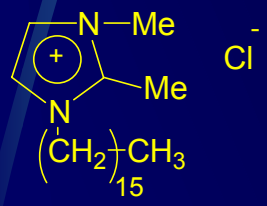
TGA of Alkyl-Imidazolium- and Alkyl Quaternary-MMT

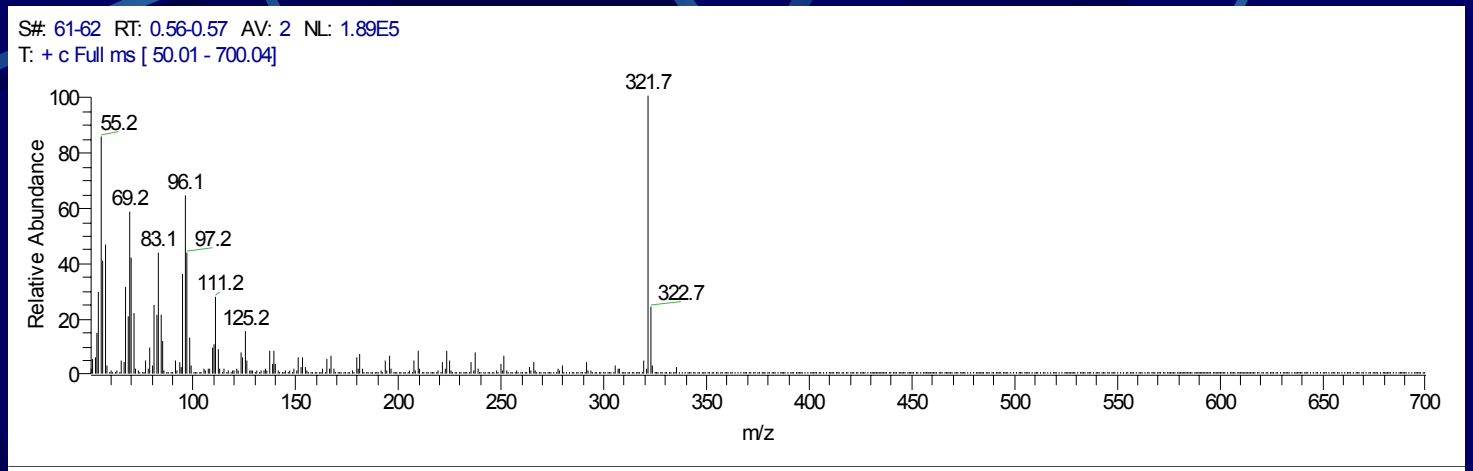
Sample	TGA, °C (N_2)		TGA, °C (air)		Imidazolium content			Δ in d-spacing vs. Na-MMT (nm)
	T_{onset}	T_{peak}	T_{onset}	T_{peak}	Theoretical	Under Air	Under N_2	
DMDODA/MMT	280	308	226	299	34.11	34.43	31.15	1.49
MHEtIM/MMT	325	492	290	482	9.39	8.65	8.10	
DMPIM/MMT	340	445	305	422	11.57	10.30	8.77	0.2
DMBIM/MMT	340	448	303	381	12.59	11.60	9.17	0.16
DMDIM/MMT	320	432	234	312	18.26	17.14	13.63	0.49
DMHDIM/MMT	343	406	250	298	23.21	23.50	20.53	0.72
DMEiIM/MMT	308	409	250	317	26.20	27.10	26.09	
DMMeOEtOEtIM/MMT	250	319	233	320				
DMEtBIM/MMT	262	418	235	384				

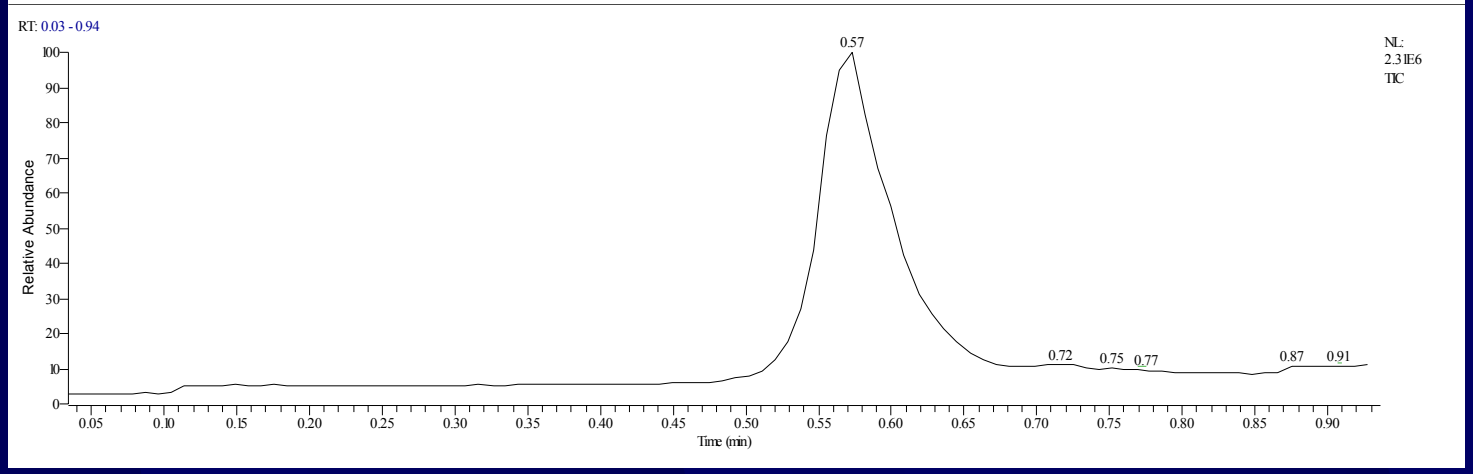
Uncertainty ± 1.2 °C (2 sigma)

BF4, ht xtr\suin

Thermal Desorption MS of DMHDIM-Cl

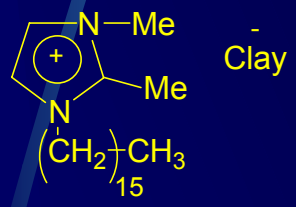


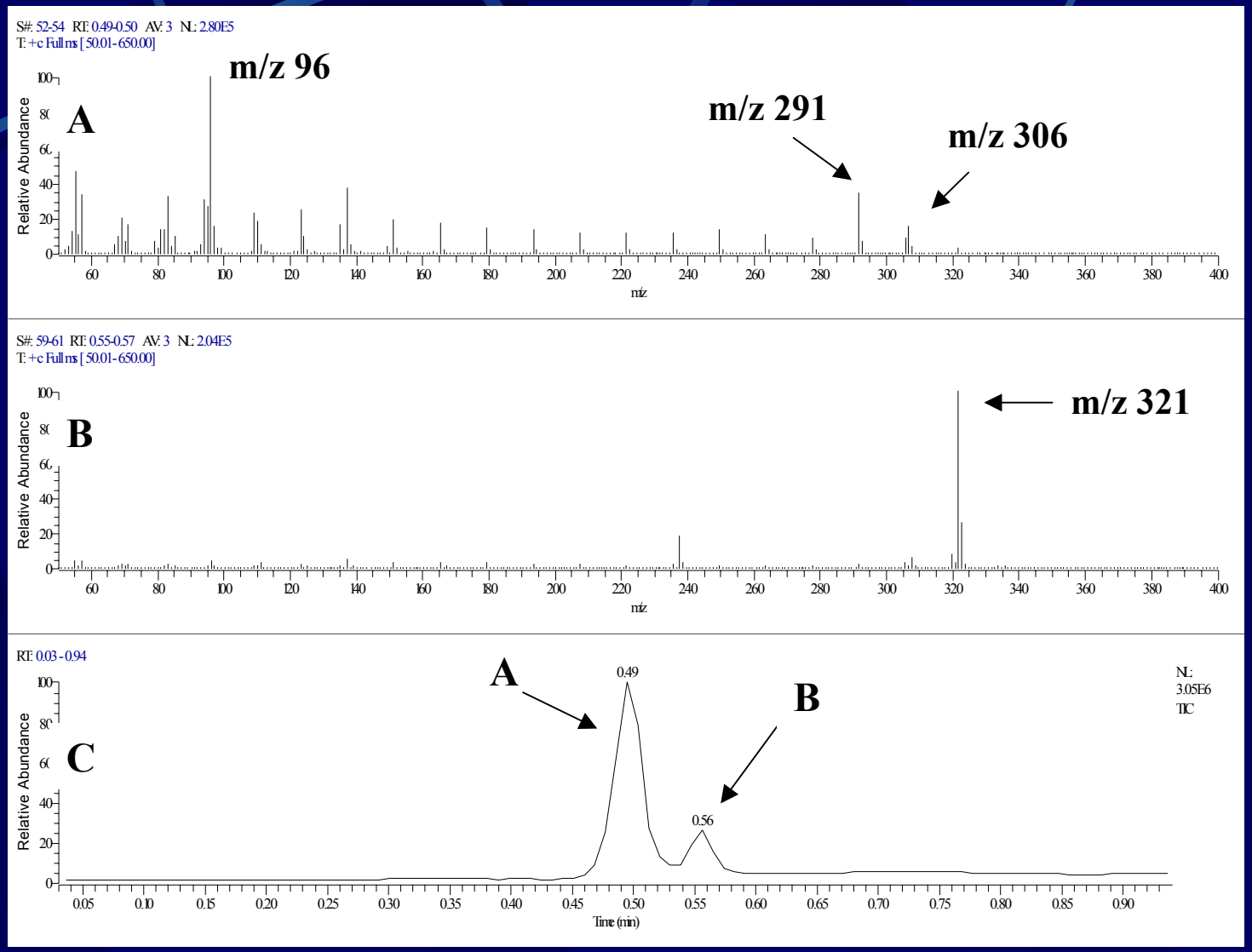




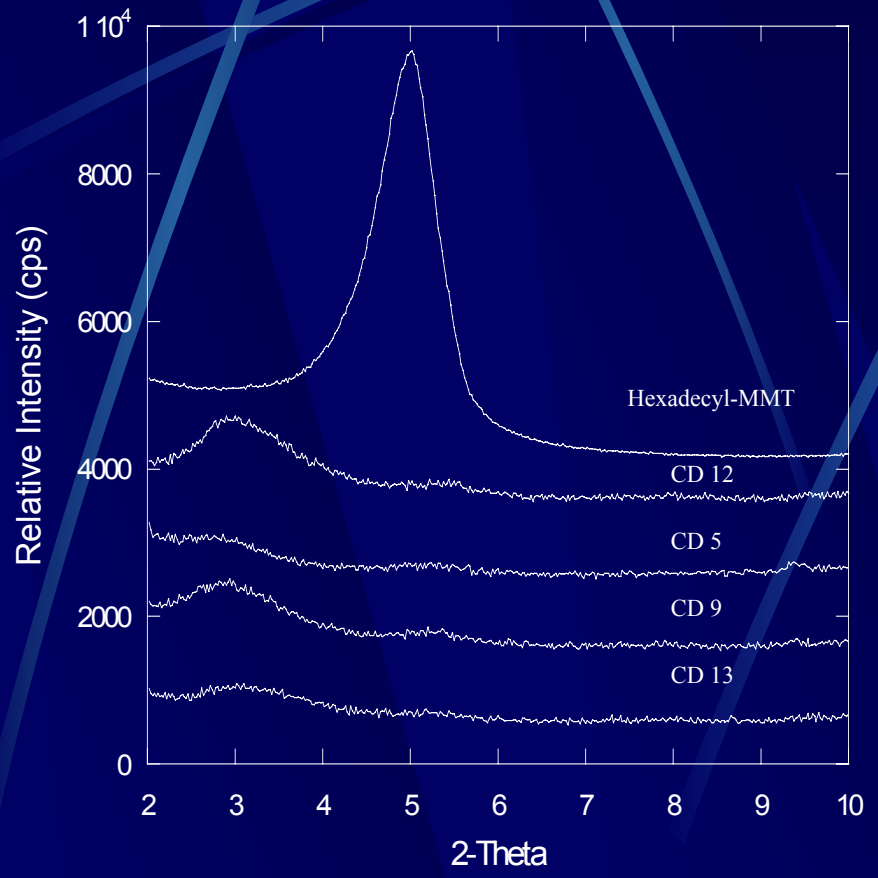
Gilman, J.W.; Awad, W.H.; Davis, R.D.; Davis, C.H.; Shields, J.R.; Harris Jr., R.H.; Morgan, A.B.; Sutto, T.E.; Callahan, J.; Trulove, P.C.; DeLong, H.C.; Polymer Layered-Silicate Nanocomposites from Thermally Stable Trialkyl Imidazolium Treated Montmorillonite, *in preparation.*

Thermal Desorption MS of DMHDIM-MMT

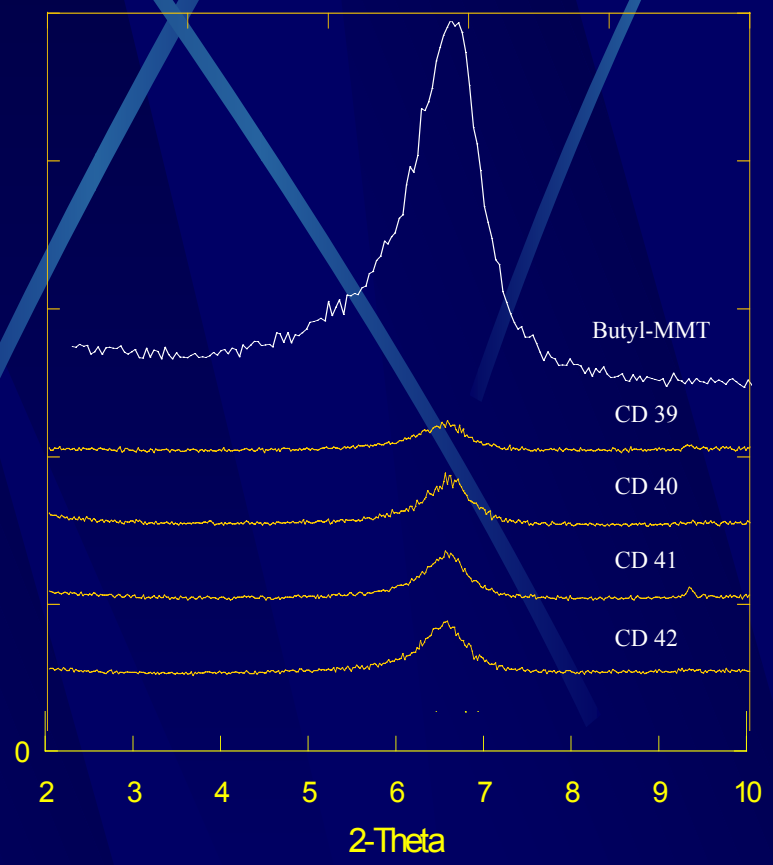




Effect of Varying Imidazolium Organic Modifier



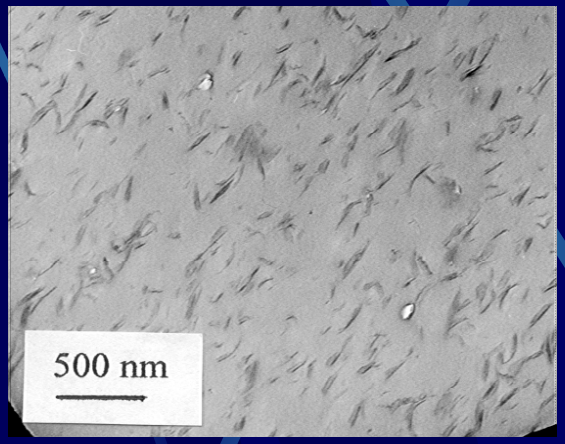
Hexadecyl-MMT/PET nanocomposites

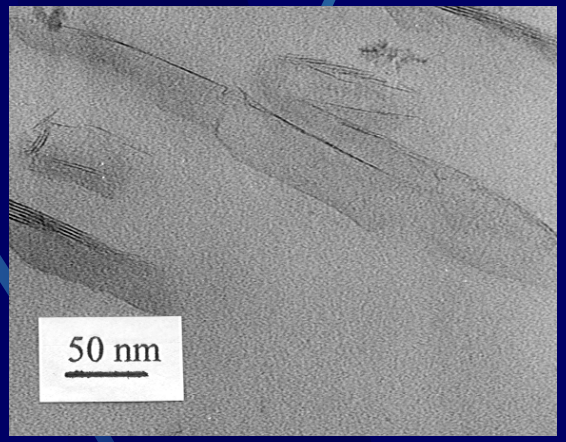


Butyl-MMT/PET nanocomposites

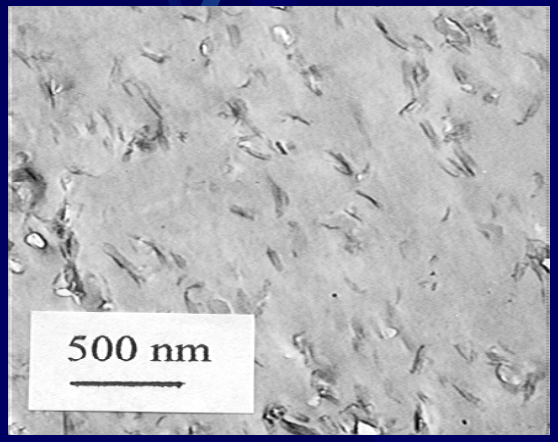
Optimal Melt Blend Processing Conditions

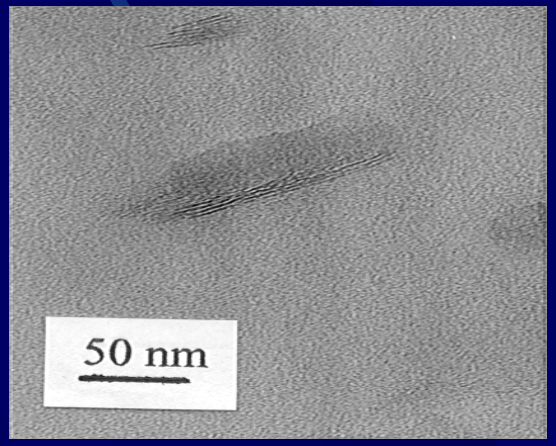
CD 12: hexadecyl-MMT/PET nanocomposite
Screw speed: 200 rpm
Residence time: 2 minutes





CD 13: hexadecyl-MMT/PET nanocomposite
Screw speed: 300 rpm
Residence time: 5 minutes





Conclusions

- Imidazolium cation is more thermally stable than alkyl ammonium cation
- Halide anion results in lower imidazolium molten salt thermal stability
- Imidazolium alkyl group influences the thermal stability of the salts
- Imidazolium-MMTs are more thermally stable than quaternary-MMT and imidazolium salt