Recent Progress in Isomeric Polyimides

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Isomeric polyimides, particularly that derived from isomeric dianhydrides continuously attract researchers' attention. This article tries to summarize the recent progress in this area.

1. Study on the difference in crystallization of polyimides derived from 4,4'-ODPA , 3,4'-ODPA and 3,3'-ODPA[1]

4,4'-ODPA/ODA with controlled molecular weight, such as inherent viscosity about 0.5dL/g trends to crystallize after annealing above 300°C. However, 3,4'-ODPA/ODA and 3,3'-ODPA/ODA did not crystallize even at temperature as high as 370°C。

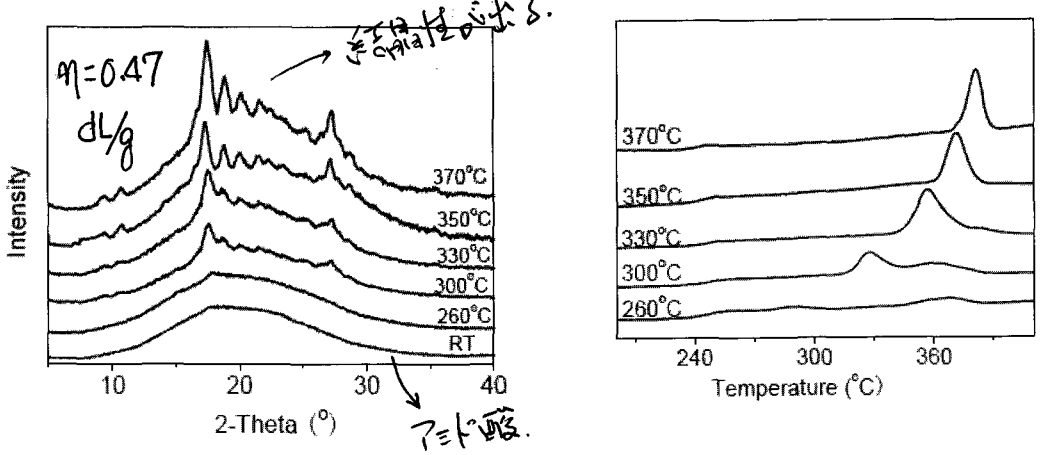


Figure 1. Polyimide of 4,4'-ODPA/ODA/PA annealed for 50 min at each temperature: WAXD(left) and DSC(right)

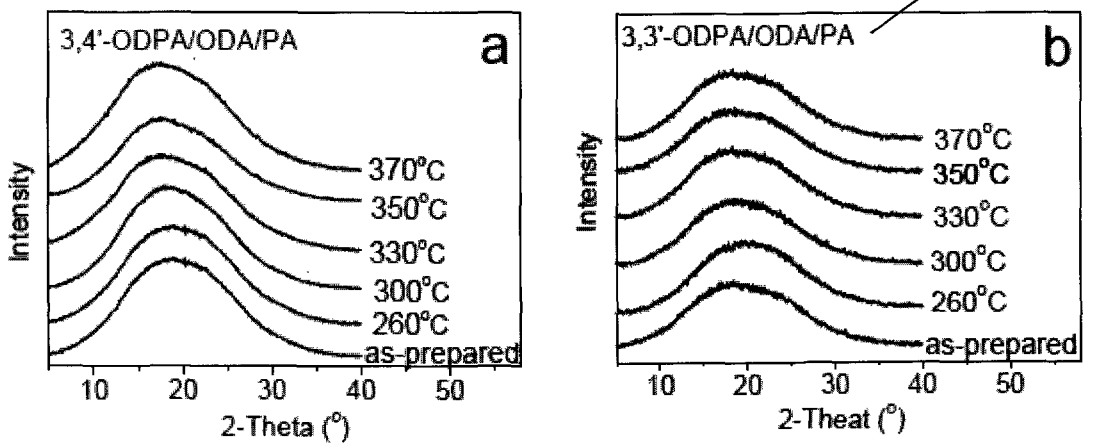


Fig. 2. WAXD for polyimides annealed for 50 min at each temperature: 3,4'-ODPA/ODA/PA(a), 3,3'-ODPA/ODA/PA(b)

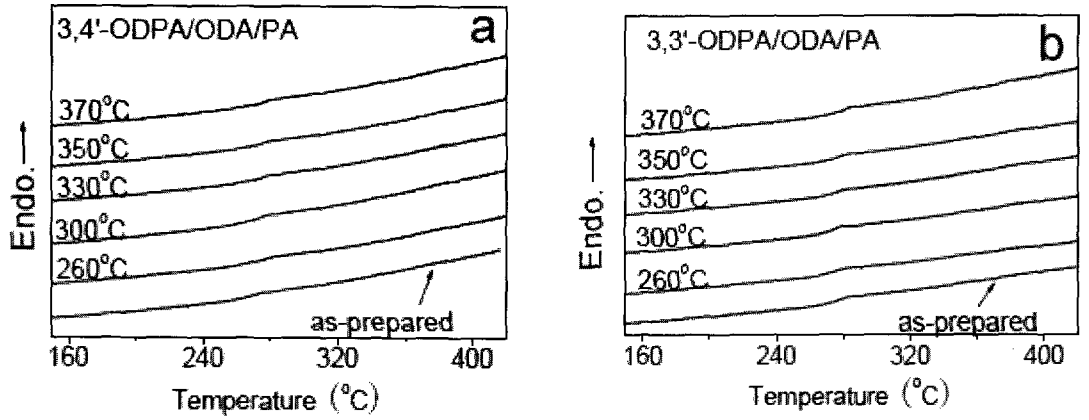
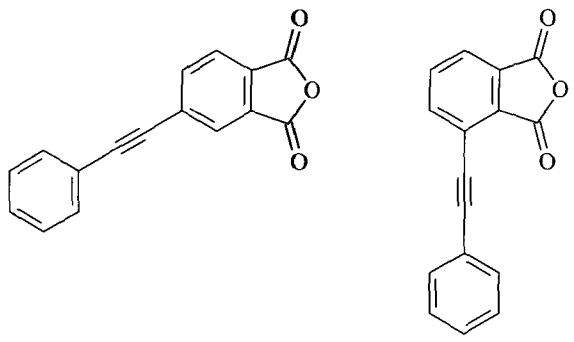


Fig. 3. DSC for polyimides annealed for 50 min at each temperature: 3,4'-ODPA/ODA/PA(a), 3,3'-ODPA/ODA/PA(b)

2. Study on 3-PEPA[2]

3-phenylethynylphthalic anhydride (3-PEPA) was synthesized and used for matrix resin for comparison with 4-PEPA. The resin from 3-PEPA may have about 20-30°C higher both at lowest melt viscosity and cross-linking temperature. It may be useful for designing a polymer with even higher Tg.



4-PEPA **3-PEPA**

Table 1. 3,4′-BPDA based matrix resins end-capped with 3- and 4-PEPA

Entry	Composition	Calc. *Mn* (g/mol)
OI-1	3,4′-BPDA/ODA/3-PEPA=1/2/2[a]	1120
OI-2	3,4′-BPDA/ODA/4-PEPA=1/2/2	1120
OI-3	3,4′-BPDA/ODA/3-PEPA=2/3/2	1579
OI-4	3,4′-BPDA/ODA/4-PEPA=2/3/2	1579

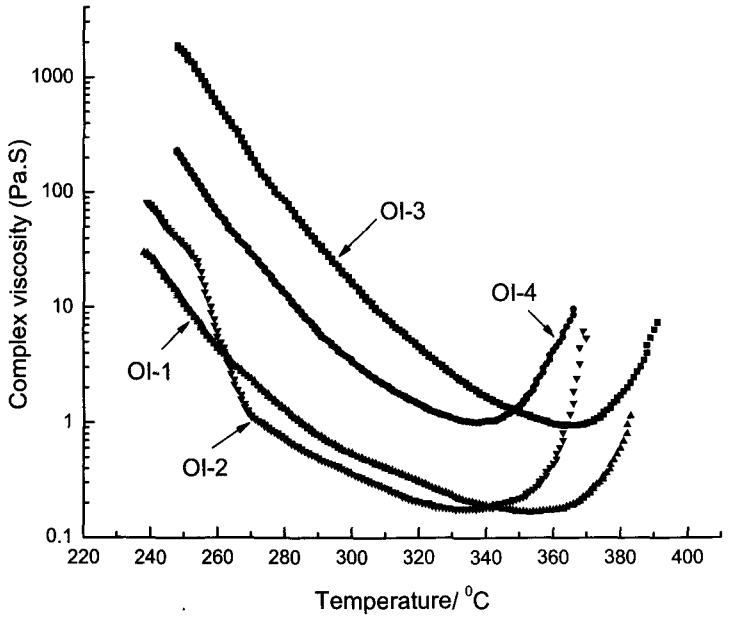


Fig. 4. Melt viscosity of 3,4′-BPDA based matrix resins end-capped with 3- and 4-PEPA

Table 2. Properties of the films polyimide end-capped with 3- and 4-PEPA with the same calculated molecular weight

PEPA	Diamine	Tg °C	T5% °C	Tensile Strength MPa	Tensile Modulus GPa	Elongation %
3-	1,3,4-APB	277	551	112	2.3	29
4-	1,3,4-APB	270	540	117	2.4	32
3-	1,3,3-APB	272	529	123	1.3	24
4-	1,3,3-APB	268	518	125	1.3	28

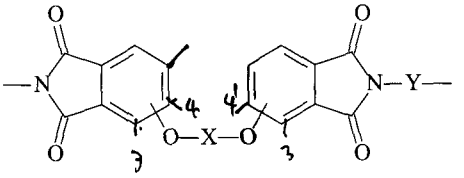
Table 3. DSC Data of model compounds

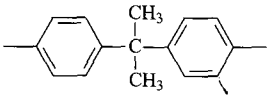
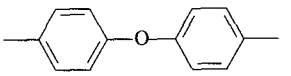
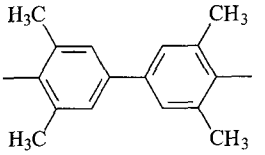
Model compound	Endo/°C	Exo/°C	
	mp	Onset	Peak
N-phenyl-3-phenylethynylphthalimide	194	320	408
N-phenyl-4-phenylethynylphthalimide	203	296	390

3. The Tgs of polyimides derived from isomeric dianhydrides [3]

The glass transition temperature of polyimides prepared from isomeric dianhydrides (with a given diamine) decreases in the order 3,3'- >3,4'- >4,4'-dianhydride. A higher Tg results from the hindrance to rotation around the bond between the bridge unit and the 3-substituted carbon of the phthalimide moiety. However, when the diamine having substituent at ortho position to the p,p'-diamino group was used, the Tg of the polyimide derived from isomeric dianhydride may have an opposite order, such as showed in Table 4.

Table 4. Tgs of the polyimides derived from diether-dianhydride and diamines



X	Location	Y	Tg/℃
	3,3'-		231
	4,4'-		215
	3,3'-		265
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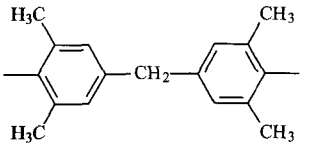
	3,3'-		223
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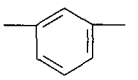
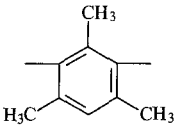
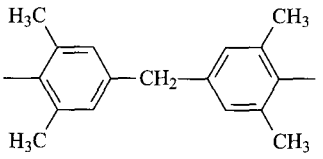
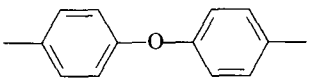
	3,3'-		219
	4,4'-		215
	3,3'-		236
	4,4'-		220
	3,3'-		270
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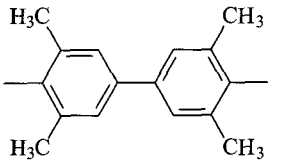
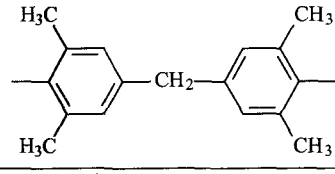
	3,3'-		276
	4,4'-		>420

	3,3'-		243
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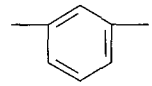
	3,3'-		269
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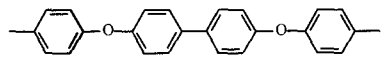
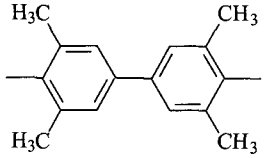
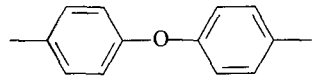
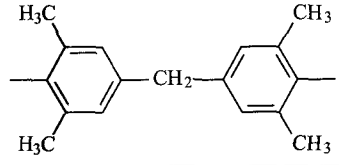
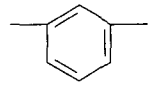
	3,3'-		259
	4,4'-		248
	3,3'-		298
	4,4'-		299
	3,3'-		289
	4,4'-		420
	3,3'-		311
	4,4'-		295

4. Study on gas separation of isomeric polyimides[4]

The polyimides based on 3,3'- or 3,4'-dianhydride usually have higher permeability and comparable or even higher permselectivity.

Table 5. Polyimides based on isomeric dianhydride for gas separation

Specimen	Film thickness	P_{H2}	P_{O2}	P_{N2}	P_{CO2}	P_{CH4}	$\alpha_{H/N}$	$\alpha_{O/N}$	$\alpha_{C2/C4}$
BTDA	μm								
4,4' /DMMDA	20	6.58	0.111	0.0272	0.851	0.0163	241.6	4.07	52.4
3,4' /DMMDA	20	6.99	0.250	0.0280	0.943	0.0171	249.1	8.93	55.3
BPDA									
4,4' /ODA	21	0.95	0.029	0.0043	0.0934	0.0020	220.2	6.68	46.7
3,4' /ODA	44	8.76	0.538	0.0823	2.66	0.0560	106.4	6.55	47.7
4,4' /APB	25	1.91	0.089	0.0134	0.431	0.0092	142.7	6.64	46.8
3,4' /APB	40	10.30	0.746	0.127	4.04	0.116	81.01	5.86	34.9
TDPA									
4,4'/ODA	28	3.64	0.155	0.0272	0.705	0.0230	133.8	5.70	30.7

3,4'/ODA	24	4.92	0.252	0.0388	1.28	0.0316	126.7	6.49	40.4
3,3'/ODA	18	6.62	0.369	0.0521	2.01	0.0398	127.0	7.08	50.4
4,4'/APB	25	4.56	0.208	0.0296	1.01	0.0236	154.4	7.05	42.9
3,3'/APB	22	7.18	0.437	0.0638	2.44	0.0514	112.7	6.86	47.6
HQDPA									
4,4'/DMMDA	25	5.95	0.222	0.0313	0.886	0.0195	190.3	7.09	45.4
3,3'/DMMDA	32	6.95	0.330	0.0612	1.33	0.0662	113.6	5.40	20,2
4,4'/APB	19	5.73	0.316	0.0470	1.54	0.0365	121.9	6.72	42.1
3,3'/APB	13	8.95	0.637	0.0970	3.52	0.0837	92.6	6.59	42.0
4,4'/ODA	19	4.24	0.203	0.0306	0.830	0.0216	138.4	6.64	38.5
3,3'/ODA	38	7.53	0.498	0.104	2.34	0.108	72.1	4.77	21.7
ODPA									
4,4'/APB	25	4.63	0.228	0.0321	1.08	0.0234	144.3	7.11	46.0
3,4'/APB	19	6.16	0.358	0.0536	1.89	0.0428	115.1	6.68	44.2
3,3'/APB	35	6.43	0.379	0.0560	1.86	0.0438	115.9	6.83	42.5
4,4'/DMMDA	41	7.01	0.250	0.0371	0.828	0.0183	188.8	6.72	45.3
3,3'/DMMDA	39	6.09	0.270	0.0377	1.1647	0.0251	161.8	7.17	46.5
4,4'/ODA	31	2.19	0.099	0.0164	0.451	0.0103	133.4	6.06	43.7
3,4'/ODA	26	5.50	0.268	0.0354	1.30	0.0360	155.2	7.58	36.1
PTPS									
4,4'/APB	28	4.80	0.254	0.0508	1.26	0.0580			
3,3'/APB	38	7.06	0.453	0.0902	2.59	0.0955			
4,4'/ODA	28	4.45	0.216	0.0473	1.07	0.0601	94.2	4.56	17.8
3,3'/ODA	24	6.64	0.400	0.0683	2.23	0.0730	97.3	5.86	30.5

5. Melt viscosity of matrix resins of oligoimides derived from isomeric dianhydrides other than BPDA [1,5]

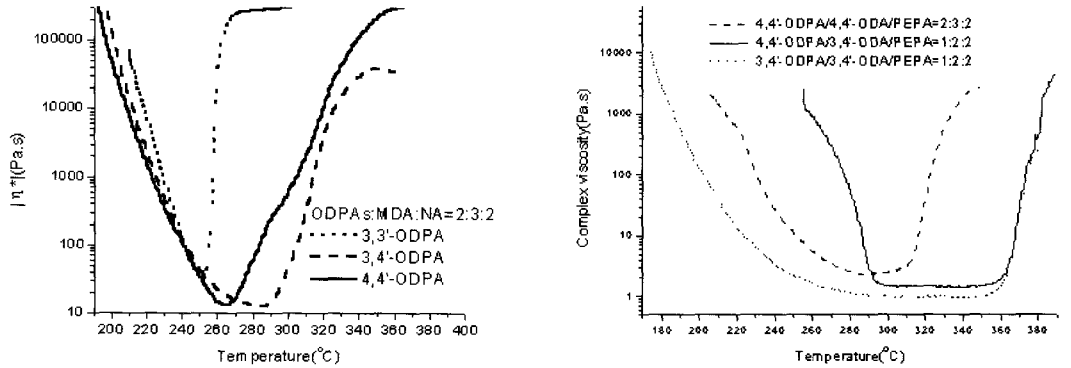


Figure 3. Polyimide matrix resins based on isomeric ODPA
End-capped with NA(left), End-capped with 4-PEPA(right)

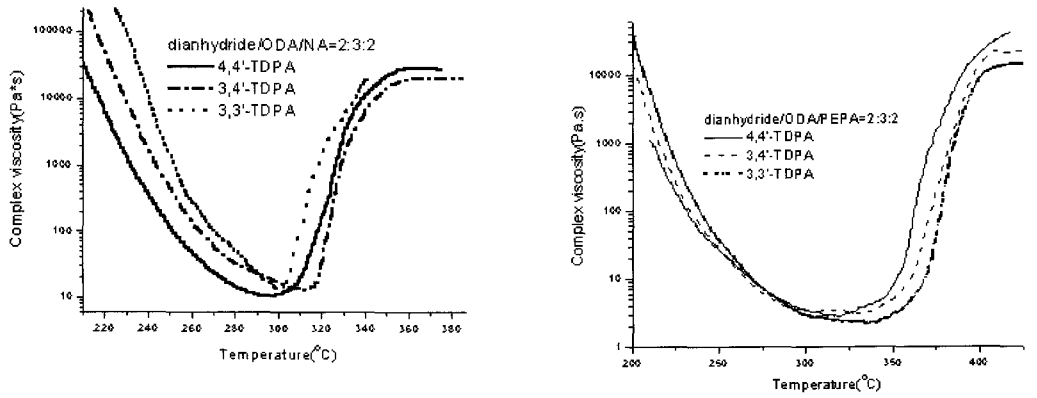


Figure 4. Polyimide matrix resins based on isomeric TDPA End-capped with NA(left), End-capped with 4-PEPA(right)

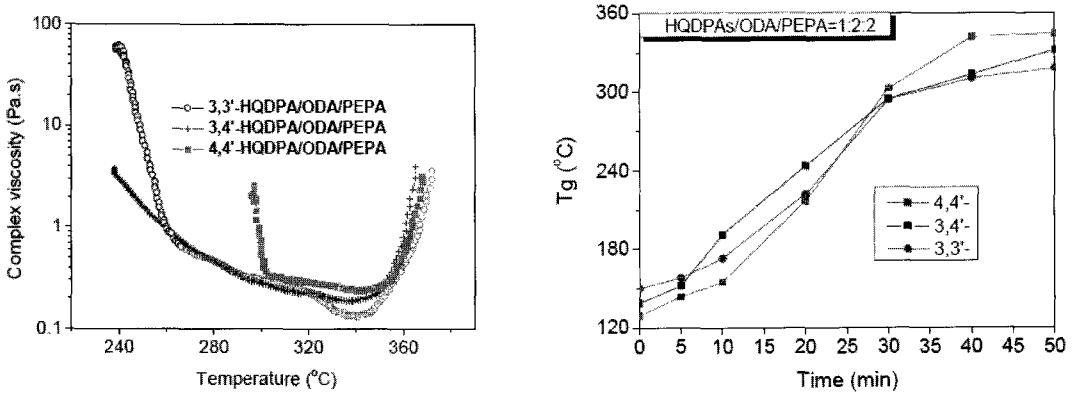


Figure 5. Polyimide matrix resins based on isomeric HQDPA Rheology(left), Tg(right)

6. Polyimides Derived from 3,3'-bis(*N*-aminophthalimide) and bis(chlorophthalimide)s[6,7]

Hydrazine as the simplest diamine was used with chlorophthalic anhydrides to synthesize polyimides. Two kinds of the polyimide have been prepared from 3,3'-bis(*N*-aminophthalimide)/dianhydride(Table 6) and bis(chlorophthalimide) /bisphenol or bisthiophenol(Table 7).

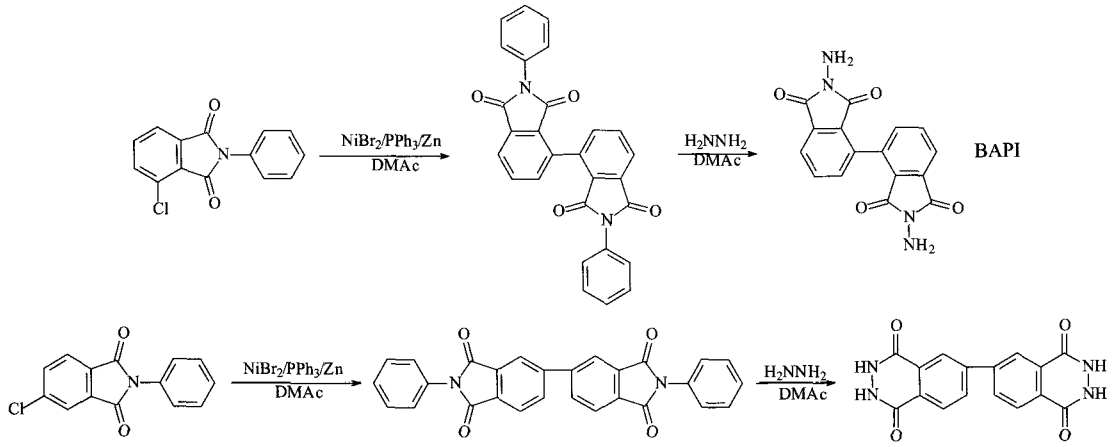


Table 6. Properties of polyimides based on BAPI

Polymer	T_g(℃)[a]	$T_{5\%}$(℃)[b]	Tensile strength(MPa)	Modulus (GPa)	Elongation (%)
BPDA/BAPI	-[c]	523	-	-	-
BTDA/BAPI	-	514	-	-	-
ODPA/BAPI	-	505	-	-	-
6FDA/BAPI	431	495	88	1.78	9.5
4,4′-HQPDA/BAPI	378	516	106	1.95	6.5
3,3′-HQPDA/BAPI	375	497	94	2.77	5.0
BPDA/BAPI/ODA	432	530	117	1.77	10.3
BTDA/BAPI/ODA	400	515	132	2.47	7.2
ODPA/BAPI/ODA	391	519	85	2.39	7.0

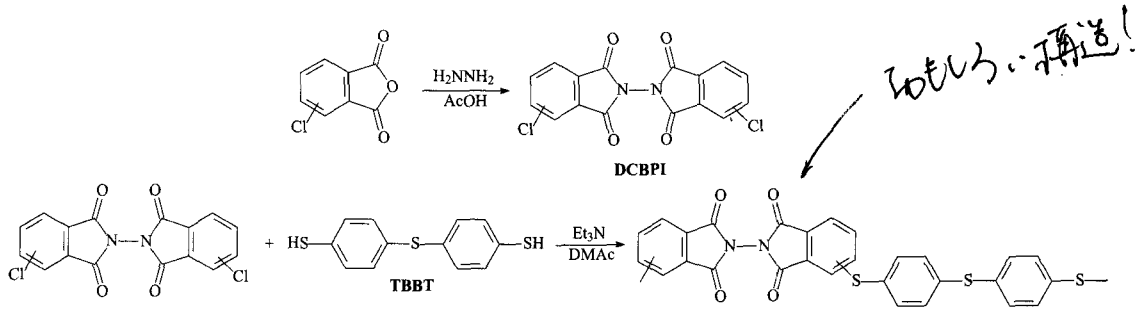


Table 7. Properties of polythioetherimides based on isomeric DCBPI

Polymer	T_g(^{0}C)		$T_{5\%}$(^{0}C)[c]	Tensile	Modulus	Elongation
	DMTA[a]	DSC[b]		strength(MPa)	(MPa)	(%)
4,4′-DCBPI/TBBT	225	222	452	117	2060	7.4
3,4′-DCBPI/TBBT	242	241	446	131	2110	8.7
3,3′-DCBPI/TBBT	263	269	455	132	2120	7.9

[a] Obtained from DMTA at heating rate of 3°C /min at 1 Hz.

[b] Obtained from DSC at a heating rate of 20°C /min in N_2.

[c] $T_{5\%}$ obtained from TGA at a heating rate of 10°C /min in N_2.

References

1. Min Zhang, PhD. Dissertation, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 2007.
2. Yanfeng Liu, Zhen Wang, Huili Yang, Lianxun Gao, Gao Li, Mengxian Ding, 3-Phenylethynyl Phthalimide End-capped Imide Oligomers and The Cured Polymers, J. Polym. Sci., Polym. Chem., in press.(→p14 for more references)