

Synthesis and Properties of Novel Sulfonated Polyimides Derived from Naphthalenic Dianhydride

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Sulfonated polyimides (SPIs) derived from 1,4,5,8-naphthalenetetracarboxylic dianhydride (NTDA) have been investigated widely due to their high performances[1], but there has few reports on SPIs based on other kinds of dianhydride[2]. A flexible dianhydride, 4,4'-Ketone dinaphthalene 1,1',8,8'-tetracarboxylic dianhydride (KDNTDA) was prepared by a new route including six steps

with an overall yield of 19 %. Several novel SPIs derived from KDNTDA were synthesized and their structures were characterized by IR and ¹H-NMR. Their reduced viscosity ranged from 0.8 to 4.5 dL/g at 35 °C. Compared to NTDA-based SPIs, KDNTDA-based ones had good solubility in common aprotic solvents not only in triethylamine salt form but also in proton form, which is favorable for processing and other operations for fuel cells. The SPIs displayed high mechanical properties

comparable to NTDA-based ones. The co-SPIs showed anisotropic membrane swelling with larger swelling in thickness than in plane. The thermal stability measurements revealed that sulfonic acid group in KDNTDA-based SPIs were stable up to 300 °C. They displayed reasonably high proton conductivity, taking their lower ion exchanging capacity (IEC) into account. The SPIs showed higher water stability and the proton conductivity values before and after aging treatment did not change. The water stability tests revealed that the SPI polymer chain scission took place mainly in the early stage but thereafter slightly.

References

[1] Y. Yin, O. Yamada, K. Tanaka, K.-I. Okamoto, *Polymer Journal*, 38(3), 197-219 (2006)

[2] X. Chen, Y. Yin, K. Tanaka, H. Kita, K.-I. Okamoto, *High Performance polymers*, in press, (2006)

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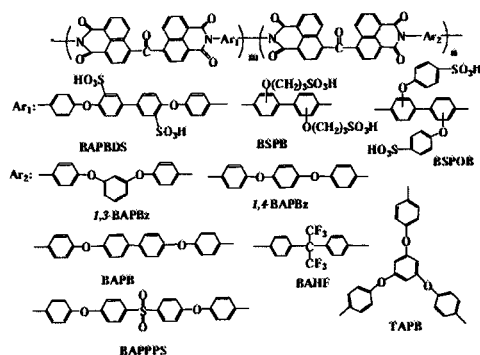


Fig 1 The structure of KDNTDA-based SPIs

Table 1 The properties of KDNTDA-based SPIs

KDNTDA-based SPIs ^a	IEC (meq/g)		η_r ^b (dL/g)	WU (%)	σ ^c (mS/cm)	DMSO ^d
	Ca.	Titr.				
K-B/1,3-BAPBz(2/1)-s	1.58	1.45	1.02	36.1	65	+
K-B/BAHF(4/1)-s	1.83	1.78	1.93	54.3	87	+
K-B/TAPB(5/4)-s	1.85	1.79	NM	41.1	110	-
K-BS/BAPBS(3/1)-r	1.62	1.59	0.8	38.6	68	+
K-BS/BAPB(3/1)-r	1.71	1.45	1.8	40.2	53	+
N-B/BAPB(2/1)-r	1.89	1.86	2.70	51	127	-
Nafion 112	0.91	0.89		39	141	

^a K-B: KDNTDA-BAPBDS, K-BS: KDNTDA-2,2'-BSPOB; ^b SPIs were in triethylamine salt form, measured at 35 °C in m-cresol; ^c Measured at 60 °C in water; ^d Solubility of SPIs, in proton form with weight concentration 5%, “+”, dissolved; “-”, undissolved.