Determination of short-chain branches in PVC by pyrolysis-hydrogenation-GC (Py-HGC)

[Background] Morphology and physical properties of PVC are known to be dependent upon the kind and amount of short-chain branches (SCB) along the polymer backbone. Here, various hydrogenation catalysts were examined for Py-HGC and several calculation methods were tested for the observed pyrograms. Experimental conditions to obtain comparable values of the kind and the amount of branches estimated by ^{13}C NMR have been established.

[Experimental] Nine PVC samples of various conversions were synthesized. They were reductively dehalogenated into PE skeletal structures using tri-n-butyltin hydride (Bu_3SnH), giving methyl(C_1), ethyl(C_2), and butyl(C_4) branches. The Py-HGC system equipped with a capillary column and with FID and MS as detector was used to pyrolyze ca. 200µg of samples at 650° under hydrogen carrier gas.The glass insert tube in the injection port was packed with hydrogenation catalyst and was maintained at 200°C. Catalysts used were 5wt% Pt, 2wt% Pd, and 5wt% Ni.

[Results]. Figure 1 shows a typical pyrogram of dehalogenated PVC (PVC-6) at 650°C where Ni catalyst is used for the in-line hydrogenation. The pyrogram that mainly consists of serial n-alkane peaks is basically the same as that of PE. Minor peaks such as 2M, 3M, and 5M in the C_{10} region are isoalkanes which reflect the branch structures in the polymer chain. Each branch content in the dehalogenated PVCs was determined by the peak simulation using well-defined ethylene-α-olefin model copolymer with known amounts of branch structure. Branch contents were calculated based on relative peak intensities of C_{10}-isoalkanes to n-decane (n-C_{10}) in the pyrograms. Calculated SCB contents are summarized in Table 1. As shown, the branch contents calculated by the C_{10} fragment data obtained by Ni catalyst proved to be much closer to those estimated by ^{13}C NMR. Also it exhibits a tendency that C_2 and C_4 contents increase with the increase of the conversion.

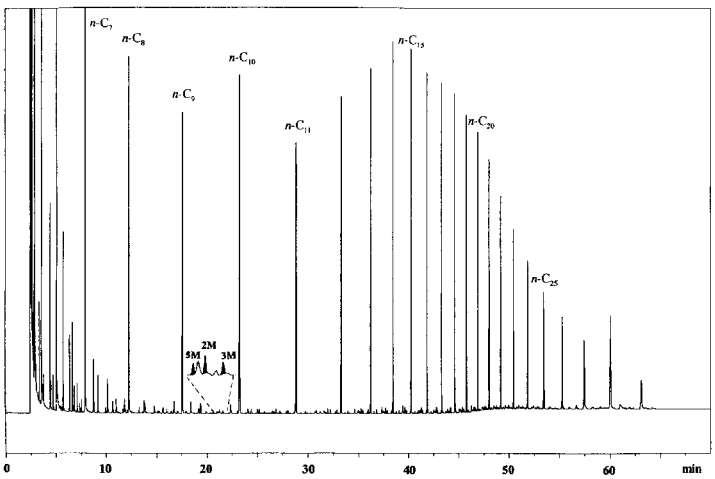

Figure 1. Typical pyrogram of a reductively dehalogenated PVC at 650°C observed after in-line hydrogenation using Ni catalyst.
Sample: PVC-6, n-C_n: n-alkane with carbon number n; 2M, 2-methylnonane, 3M, 3-methylnonane, 5M, 5-methylnonane.

Table 1. SCB contents in PVC obtained by Py-HGC using hydrogenation catalysts together with reference data obtained by ^{13}C NMR.

Fragment region	Sample	Conv. (%)	Branch contents/1000 chloride monomers		
			Ni		
			C1	C2	C4
C_{10}	PVC-1	6.3	1.8(1.6)	0.5(0.2)	0.4(0.3)
	PVC-2	10.2	2.5(3.0)	0.5(0.3)	0.7(0.5)
	PVC-3	22.6	3.8(5.0)	0.7(0.5)	1.0(0.7)
	PVC-4	38.5	3.2(4.1)	0.9(0.5)	1.1(0.8)
	PVC-5	55.1	3.2(3.1)	0.9(0.4)	1.1(0.8)
	PVC-6	70.1	3.4(3.6)	1.0(0.7)	1.1(0.7)
	PVC-7	81.0	3.6(4.1)	1.0(0.8)	1.2(0.7)
	PVC-8	86.7	3.8(3.7)	1.1(0.8)	1.6(1.5)
	PVC-9	93.5	4.2(4.4)	1.4(1.1)	1.7(1.7)

* The SBC contents determined by ^{13}C NMR are given in parentheses.

*Contents excerpted from S. Mao, H. Ohtani, S. Tsuge, H. Niwa, M. Nagata, *Polymer J.* Vol. 31, No.1 79-83 (1999)

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Applications : General polymer analysis

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