

## A novel approach to the characterization of end groups in styrene-methyl methacrylate copolymers by Py-GC

**[Background]** NMR has been extensively used for the characterization of end groups of polymers because of its ability to obtain information on end groups as well as adjacent moieties. However, its sensitivity and dynamic range are often insufficient for the quantitative analysis of end groups in copolymers. Here, end groups and adjacent structures in St-MMA copolymer chains were investigated by Py-GC and Py-GC/MS.

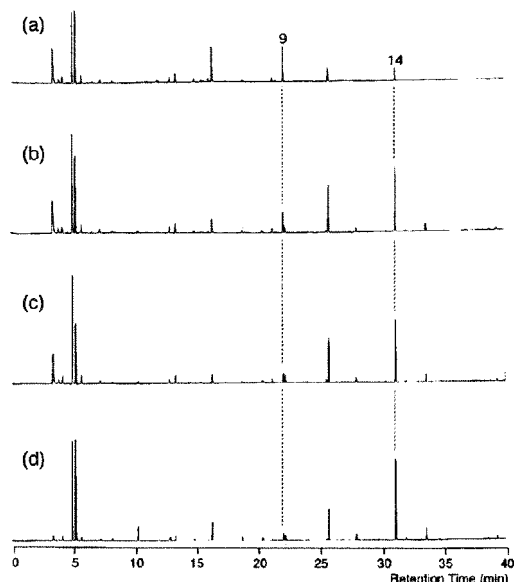
**[Experimental]** The St-MMA copolymers were synthesized by radical polymerization with AIBN as an initiator. Py-GC measurements were carried out on a GC equipped with an FID. To confirm the characteristic products of AIBN residues at the chain ends, a nitrogen phosphorous detector (NPD) was also used. About 100µg of polymer samples was pyrolyzed under a flow of He at 550°C with a vertical microfurnace pyrolyzer directly attached to the injection port of GC. Identification of peaks on the pyrograms was carried out by GC/MS to which the pyrolyzer was also attached.

**[Results]** As shown in Table 1, the observed N values (average number of initiator residues) were between C-1 and C-2 suggesting the estimated molar abundance for recombination was between 56 and 77%. This suggests that the polymerization process for the given copolymer samples terminated preferentially by recombination. The previously reported ratios between recombination and disproportionation, 95/5 for PS and 15/85 for PMMA, support the observed predominance of recombination over disproportionation. Figure 1 shows pyrograms of the three model blends and a copolymer (C-2) detected by NPD. Comparison of the intensities of peaks 9 and 14 suggests that recombination between the isobutyronitrile radical and each monomer radical occurred during pyrolysis. However, pyrogram (d) was quite similar to pyrogram (c). Thus, the monomer units adjacent to the end-group AIBN residues would mostly consist of styrene, despite the copolymer composition (St/MMA=1/1).

**Table 1.** Average number of initiator residues (N) in one molecule of copolymers and ratio between recombination and disproportionation termination

Sample code	Mn by (SEC)	N <sup>a</sup>	Estimated abundance (mol %)	
			Recombination	Disproportionation
C-1	13,500	1.56	56	44
C-2	23,800	1.68	68	32
C-3	60,600	1.77	77	23

<sup>a</sup> Experimentally calculated.



**Figure 1.** Pyrograms of model mixtures of homopolymers and the copolymer (C-2) detected by NPD: (a) 1:1 mixture of PMMA-A and PS-B with end group AIBN adjacent to MMA, (b) equal amount mixture of four homopolymers: PMMA-A, PMMA-B, PS-A, and PS-B, (c) 1:1 mixture of PMMA-B and PS-A with adjacent units is St, (d) Copolymer (C-2)

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**Keyword :** Styrene-methylmethacrylate copolymer, End group, Py-GC

**Applications :** General polymer analysis

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