Tacticity of methacrylic copolymers studied by Py-GC

[Background] Methacrylic polymers and their crosslinked polymers are widely used for industrial thermoplastics. The control of stereoregularity of these polymers is often required to obtain a needed performance, such as glass transition temperature (Tg) which depends on the tacticity of methacrylic polymers. Here, the Py-GC technique was applied to determine the tacticity of various PMMA copolymers, including crosslinked ones otherwise it had been difficult to evaluate the stereoregularity.

[Experimental] About 0.1% of initiator was used to effect radical polymerization of methyl methacrylate (MMA). The tacticity of linear polymers was estimated by ^{1}H-NMR by use of α-methyl proton resonance. The Py-GC measurements were carried out with a GC equipped with an FID and a vertical microfurnace type pyrolyzer (PY-2010SL, Frontier Lab). About 0.2mg of polymer samples was pyrolyzed at 500ºC under a flow of He carrier gas.

[Results] Figure 1 shows the pyrogram of PMMA obtained at 500ºC together with a view of expanded tetramer region. The MMA tetramers consist of two isomers (A and B), each of which has a pair of diastereomers (Am and Ar, and Bm and Br, respectively) where m and r designate meso- and racemo isomers, respectively. The diad tacticity of MMA-MA copolymer was also determined by Py-GC from the intensities of the diastereomeric MMA tetramers in the observed pyrograms of the copolymer. The diad tacticity values for the MMA-MA copolymers determined from the relative peak intensities of the diastereomeric MMA tetramers and those obtained by ^{1}H-NMR are compared in Table 1. The diad tacticities observed by Py-GC agree well with those obtained by ^{1}H-NMR with one exception for S-10 which had a higher MA content (30%). ^{1}H-NMR did not allow accurate determinations because of poorly resolved spectra caused by the strong effect of MA sequences. On the other hand, the Py-GC is not affected by presence of the comonomer. Therefore, the MMA sequences in the polymer chains are selectively estimated by Py-GC, giving highly precise determinations of the tacticity, independent of the comonomer compositions.

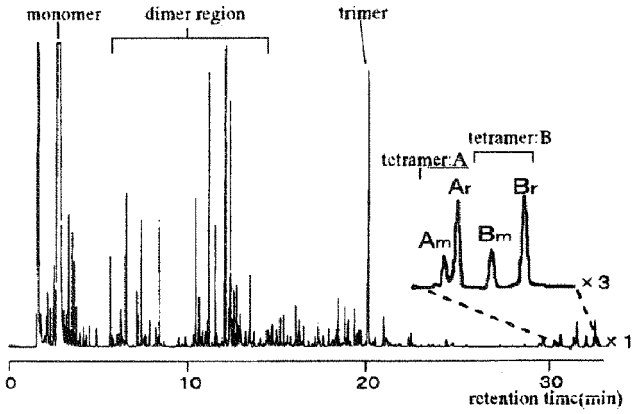

Figure 1. Pyrogram of PMMA at 500°C observed by FID

Sample	Diad tacticity (m%)		
	Py-GC	MA content (%)	^{1}H NMR
S-6	20.5	0.5	20.5
S-7	21.8	0.5	22.0
S-8	23.7	4	23.4
S-9	24.4	15	24.5
S-10	24.6	30	28.6
S-11	25.1	6	25.0
S-12	25.8	6	25.7
S-13	28.6	1	28.6

Table 1. Comparison of diad tacticity (m%) values in MMA sequences of MMA-MA copolymers determined by Py-GC and by ^{1}H-NMR

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