Studies on End Groups in Radically Polymerized Poly(methyl methacrylate) (PMMA) by Py-GC

[Background] It is known that subtle differences of the chain ends of a polymer can cause significant changes in property of the polymer such as thermal stability and transparency. Also, the chain end information provides excellent clues for the polymerization mechanism. However, the identification and determination of of end groups is no easy task because of complexity and low concentration. In this work PyGC technique was used to characterize the end groups of PMMA samples which had been radically polymerized in toluene with BPO.

[**Experimental]** PMMA samples were prepared by a standard procedure. A vertical microfurnace pyrolyzer was directly attached to a GC with an FID. 0.5mg of the polymer sample was pyrolyzed at 460˚C under nitrogen. A fused silica capillary column coated with polydimethylsiloxane was used for GC separation of pyrolyzates. Identification of peaks on the pyrograms was done using a GC-MS to which the pyrolyzer was directly attached.

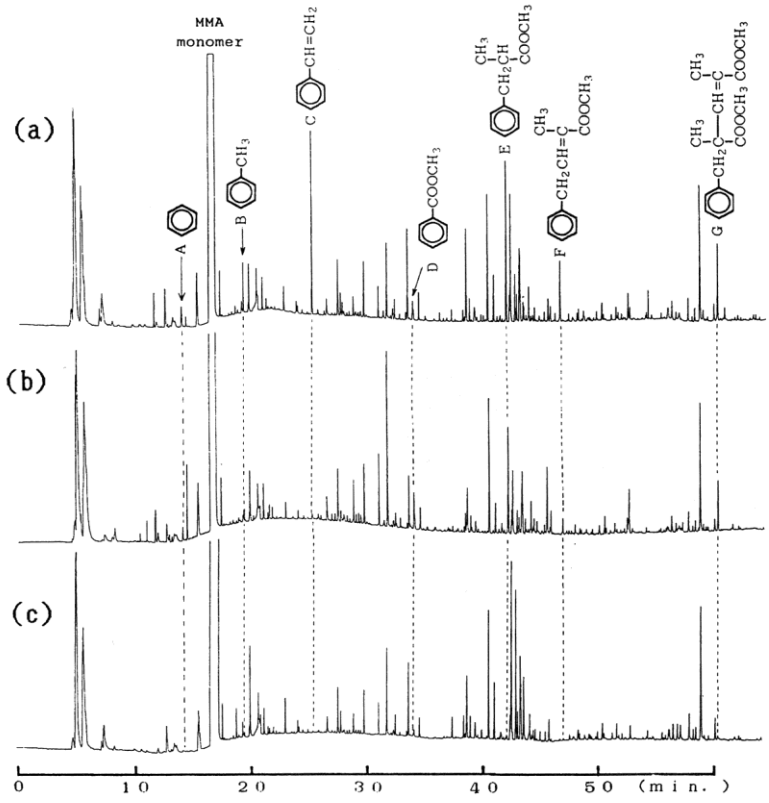

Figure 1. Pyrograms of PMMA samples at 460˚C; (a) polymerized in toluene, (b) polymerized in benzene, and (c) polymerized without any initiator.

[Results] Figures 1a, b and c show the pyrograms of PMMA samples polymerized with 0.3% of BPO as the initiator in toluene, in benzene, and thermally polymerized without any reagents, respectively. Generally, the main pyrolysis product (>95%) is the MMA monomer formed through the depolymerization reaction. Among these, several peaks (A through F) on the pyrogram (a) are identified as the products having a phenyl ring, all of which are scarcely observed on the pyrogram (c). Also, peaks B (toluene), C (styrene) and F are exclusively observed in (a). Therefore, these three products should be derived mainly from the solvent fragments incorporated into the chain ends through the chain transfer to toluene. On the other hand, initiator-incorporating chain ends are divided into two groups be-cause the thermal dissociation of BPO provides both benzoyloxy and phenyl radicals. Thus peaks E and G should be related to phenyl-initiated chain ends while peak D is related to benzoyloxy-initiated ones.

*Contents excerpted from H. Ohtani, M. Tanaka, S. Tsuge, *J.Anal. Appl. Pyrolysis* **15**, 167-174, (1989)

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1-8-14 Saikon, Koriyama
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Phone: (81)24-935-5100 Fax: (81)24-935-5102

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