Characterization of Polymerization Reagents Incorporated into Poly(methyl methacrylate) Chains by Py-GC

[Background] In radical polymerization, the fragments of initiators are incorporated into the resulting polymer chains as end groups. The end groups formed sometimes greatly affect the properties of the polymers. However, the characterization of polymerization reagents incorporated into polymers is not easy because of the low concentrations. Pyrolysis-gas chromatography (PyGC) is a simple, but extremely sensitive technique which often provides unique structural information to that obtained by spectroscopic methods.

[**Experimental]** PMMA samples were prepared both with and without polymerization reagents. A vertical micro-furnace pyrolyzer maintained at 460˚C was directly attached to a GC with an FID or a flame photometric detector (FPD). A fused silica capillary column coated with polydimethylsiloxane was used. Identification of peaks on the pyrograms was done using a GC-MS with both EI and CI sources to which the pyrolyzer was directly attached.

[Results] Figure 1 shows the pyrograms of samples prepared both (a) in the presence and (b) in the absence of polymerization reagents at 460˚C. Since PMMA tends to depolymerize mostly into the original monomer at elevated temperatures around 500˚C, the main pyrolysis product on the pyrograms (>90%) was the MMA monomer. The peak assignments are summarized in Table 1 along with their molecular weights and estimated structures obtained by PyGC-MS. As noted, peaks A through I are not observed on the pyrogram (b). Therefore, they can be assigned to the fragments of the polymerization reagents incorporated into the polymer chain.

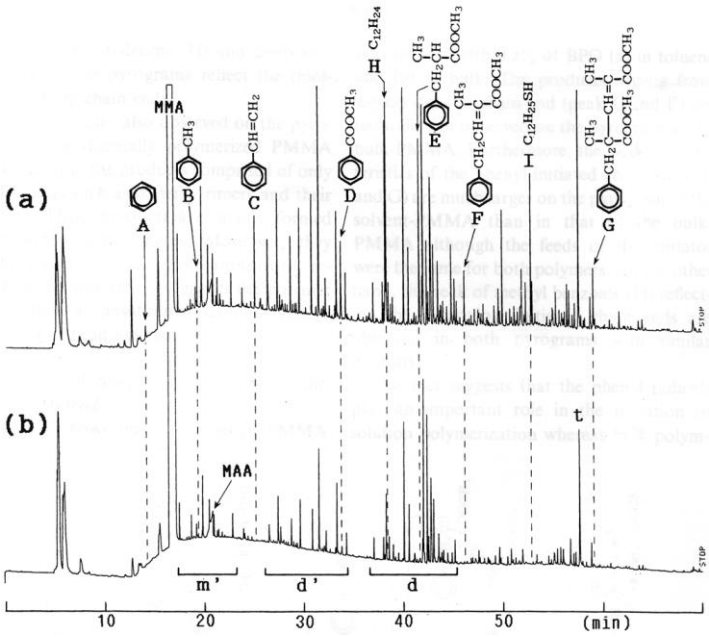

Figure 1. Pyrograms of poly(methyl methacrylate): (a) prepared in toluene with 0.3% of benzoyl peroxide and 1.5% of dodecanethiol; and (b) thermally polymerized in bulk without any polymerization reagent.

Notation[a]	MW	Estimated structure
		[from aromatic chain ends]
A	78	
B	92	$-CH_3$
C	104	$-CH=CH_2$
D	136	$-COOCH_3$
E	178	$-CH_2CH(CH_3)COOCH_3$
F	190	$-CH_2CH=C(CH_3)COOCH_3$
G	276	$-CH_2C(CH_3)(COOCH_3)CH=C(CH_3)COOCH_3$
		[from thiol-derived chain ends]
H	168	$C_{12}H_{24}$ (1-dodecene)
I	216	$C_{12}H_{25}SH$ (dodecanethiol)
		[compounds consisting of one MMA unit]
MMA	100	$CH_2=C(CH_3)COOCH_3$
m'	114	$CH_3CH=CHCH_2(COOCH_3)$ etc.
	116	$(CH_3)_3CCOOCH_3$ etc.
MAA	86	$CH_2=C(CH_3)COOH$
d'	140	$CH_2C(CH_3)CH=C(CH_3)COOCH_3$ etc.
	142	$CH_2=C(CH_3)CH_2CH(CH_3)COOCH_3$ etc.
	156	$CH_2=C(CH_3)CH_2C(CH_3)_2COOCH_3$ etc.
	158	$(CH_3)_2CH-CH_2C(CH_3)_2COOCH_3$ etc.
		[MMA dimers]
d	186	$CH_3CH(COOCH_3)CH=C(CH_3)COOCH_3$ etc.
	188	$CH_3CH(COOCH_3)CH_2CH(CH_3)COOCH_3$ etc.
	200	$(CH_3)_2C(COOCH_3)CH=C(CH_3)COOCH_3$ etc.
	214	$CH_3CH=CHC(CH_3)(COOCH_3)CH_2CH_2COOCH_3$ etc.
		[MMA trimer]
t	300	$(CH_3)_2C(COOCH_3)CH_2C(CH_3)(COOCH_3)CH=C(CH_3)COOCH_3$

Table 1 Peak assignment in the pyrograms of PMMA estimated by PyGC-MS

*Contents excerpted from H. Ohtani, S. Ishiguo, M. Tanaka, S. Tsuge, *Polym. J.* 1989, 21, 41-48

Keywords : Pyrolysis, PyGC-MS, PMMA, Polymerization Reagent

Products used : Multi-functional pyrolyzer

Applications : : General polymer analysis

Related technical notes :

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