Complex compositions of polymeric materials studied by Pyrolysis-GC/MS

Hajime OHTANI
Nagoya University, JAPAN

Analytical Pyrolysis

Characterization of polymers by Py-GC/MS

A. Identification of polymeric materials

B. Structural characterization of polymers
- (a) composition
- (b) average MW/MW distribution
- (c) monomer enchainments along polymer chains
- (d) chain-end structures
- (e) branching structures
- (f) stereoregularity
- (g) sequence distributions in copolymer chains
- (h) degree of cure / cross-linking
- (i) others

C. Mechanisms and kinetics of polymer degradation

Menu:

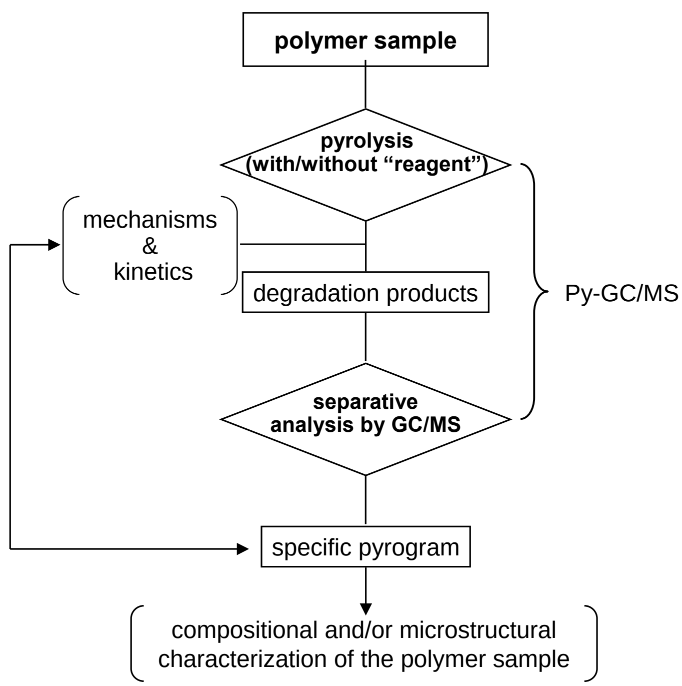
1. Brief instrumental and methodological aspects of modern Py-GC/MS

2. Recent topics in characterization of polymeric materials

   (A) Stereoregularity in vinyl-type polymers

   (B) End Groups in PMMA and polystyrene

   (C) Network structure in intractable crosslinking polymers (using thermally-assisted chemolysis)



Important factors affected the progress in polymer characterization by Py-GC/MS

A. Highly specific pyrolysis:
- (a) Curie-point pyrolyzer
- (b) Flash-filament pyrolyzer
- (c) Vertical-furnace pyrolyzer

B. High-resolution capillary columns for GC:
- (a) Glass capillary columns
- (b) Fused-silica capillary columns
- (c) Deactivated stainless steel capillary columns

C. Highly sensitive and/or selective detectors for GC:
- (a) Universal detector for C-containing compounds(FID)
- (b) Specific detectors: FPD(for S and P)
  NPD (for N and P)
  ECD (for halides), etc.

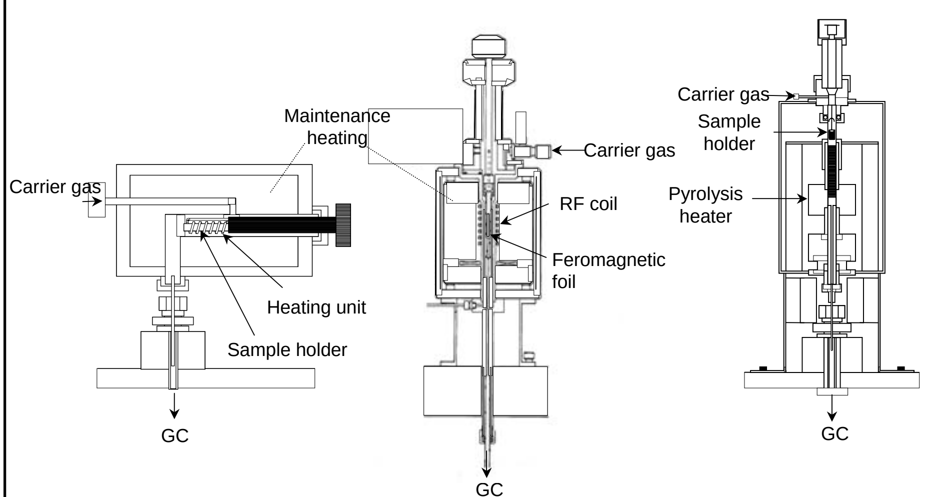
D. Specific peak identification methods on pyrograms:
- (a) Py-GC/MS
- (b) Py-GC/FTIR
- (c) Py-GC/AED, etc.

E. Thermally assisted chemolysis:
- (a) On-line hydrogenation
- (b) On-line methylation
- (c) Catalysis-assisted thermolysis, etc.

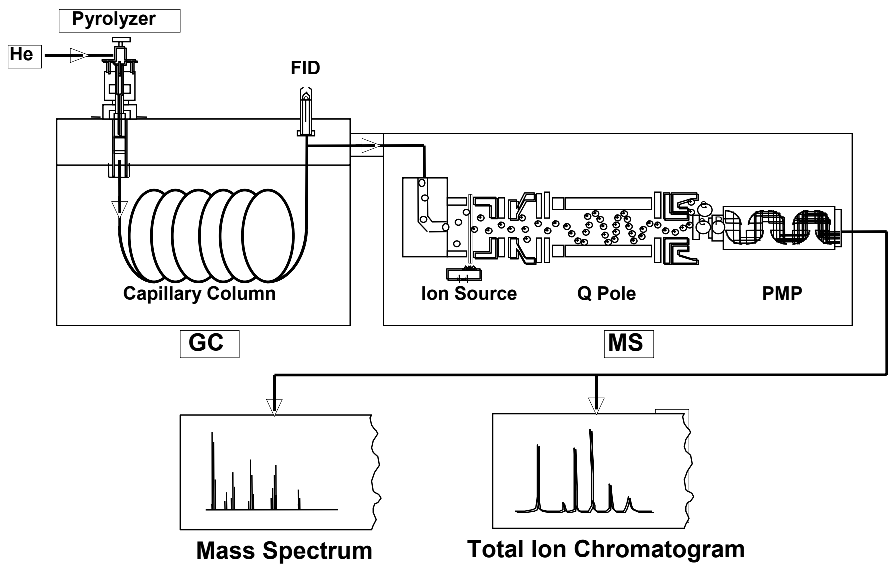
F. Computer-assisted data processing and chemometrics

Schematic diagrams of typical pyrolyzers

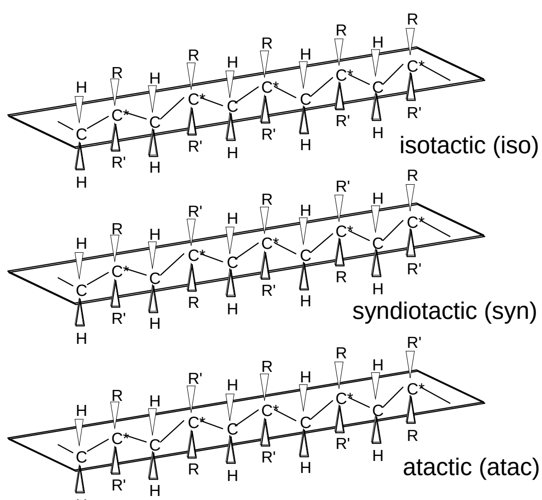
Filament pyrolyzer | Curie-point pyrolyzer | Microfurnace pyrolyzer



Typical Py-GC/MS measuring system

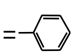


Stereoregularity of Vinyl Polymers



(C*: asymmetric carbon)

Polystyrene [PS]

R =  R' = - H

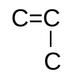
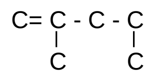
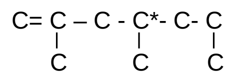
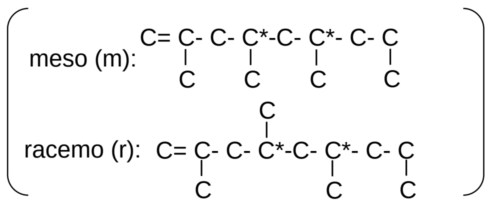
Polypropylene [PP]

R = - CH_3 R' = - H

Poly(methyl methacrylate) [PMMA]

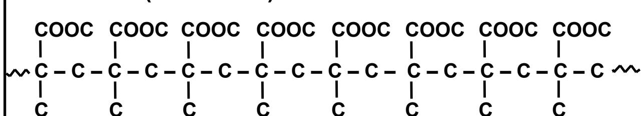
R = -C(=O)-OCH_3 R' = - CH_3

Stereoregurality of PP is only reflecting on the diastereometric fragments with more than two asymmetric carbons (larger than tetramers)

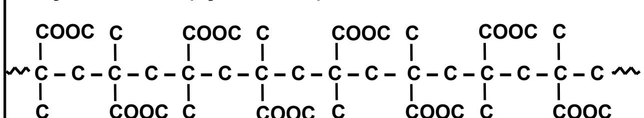
fragments	chemical structure(s) [asymmetric C:C*]	enantiomers	diastereomers
monomer		X	X
dimer		X	X
trimer		O	X
tetramer		O	◎

Stereoregularity in PMMA

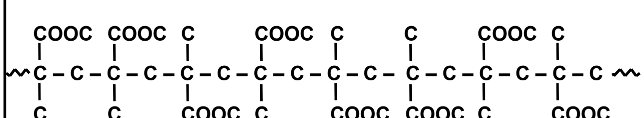
□ **isotactic (iso-PMMA)**



□ **syndiotactic (syn-PMMA)**



□ **atactic (at-PMMA)**



Samples

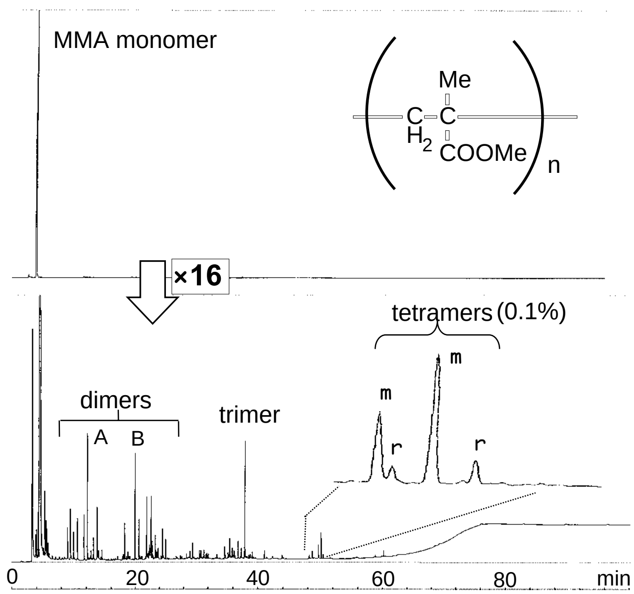
iso-PMMA

syn-PMMA

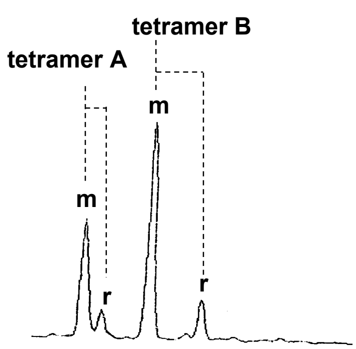
at-PMMA(isotactic rich)

at-PMMA(syndiotactic rich)

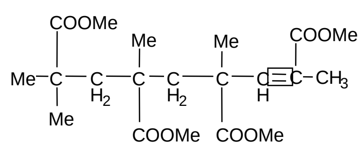
Pyrograms of at-PMMA (isotactic rich) at 500°C



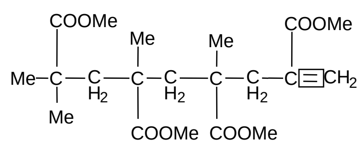
Peak assignment of tetramers in pyrogram of PMMA



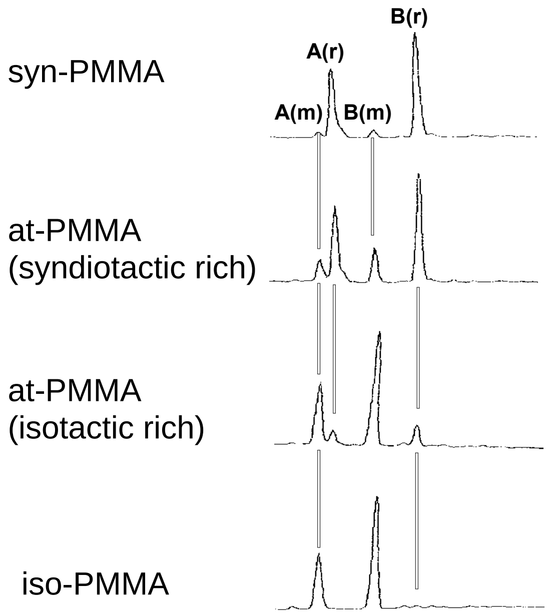
tetramer A (m)



tetramer B (m)



Tetramer region in PMMA pyrograms



Stereoregularity of PMMA

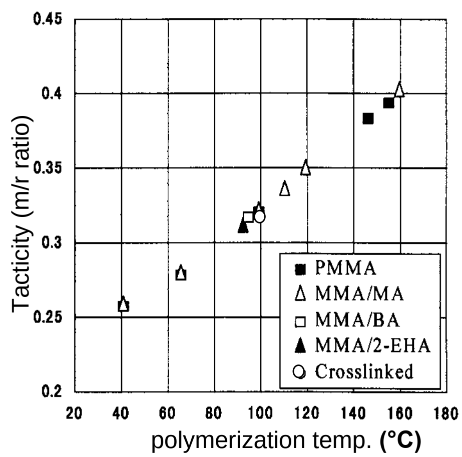
Diad tacticity of PMMAs

Sample	meso (%) Py-GC	meso (%) ^{1}H-NMR
syn-PMMA	7.4	5.6
at-PMMA (syndiotactic rich)	24.1	24.0
at-PMMA (isotactic rich)	81.8[a]	82.8
iso-PMMA	97.3	97.2

[a]C.V. for 8 runs 2.0%

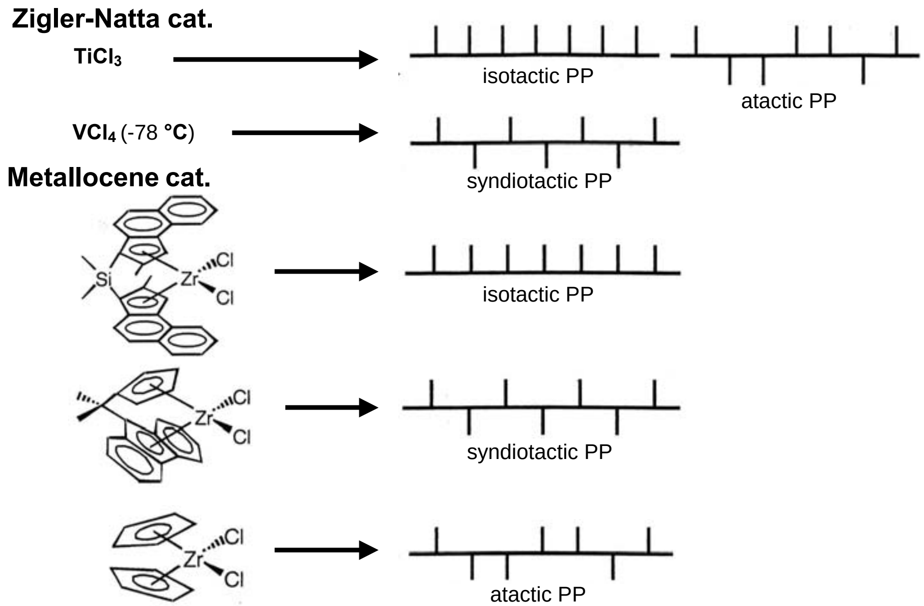
[*Macromolecules,* 30, 4891(1997)]

Relationship between tacticity and polymerization temperature

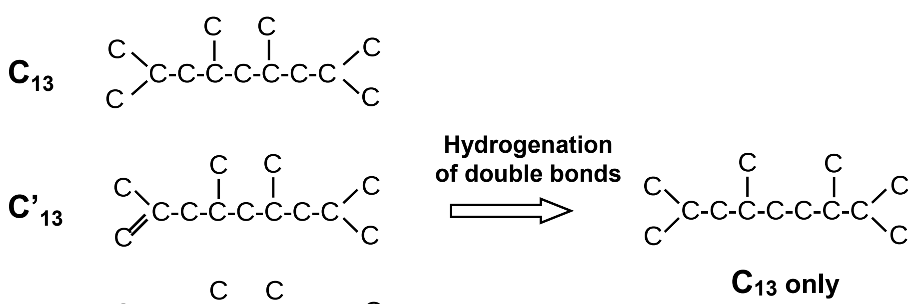


[*J. Appl. Polym. Sci.,* 78, 2140 (2000)]

Polymerization catalysts and resulting stereoregularities of polypropylenes

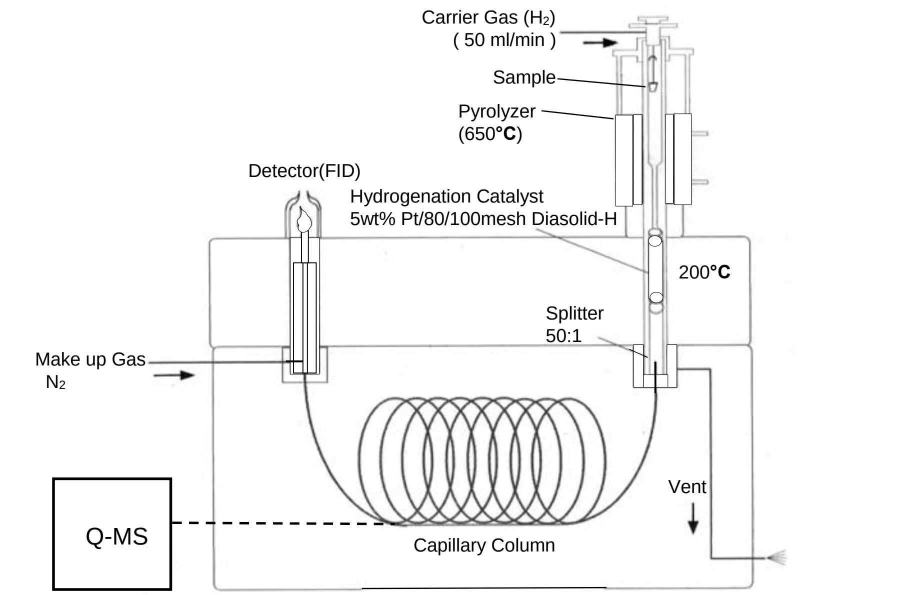


Simplification of Observed Pyrograms through in-line Hydrogenation



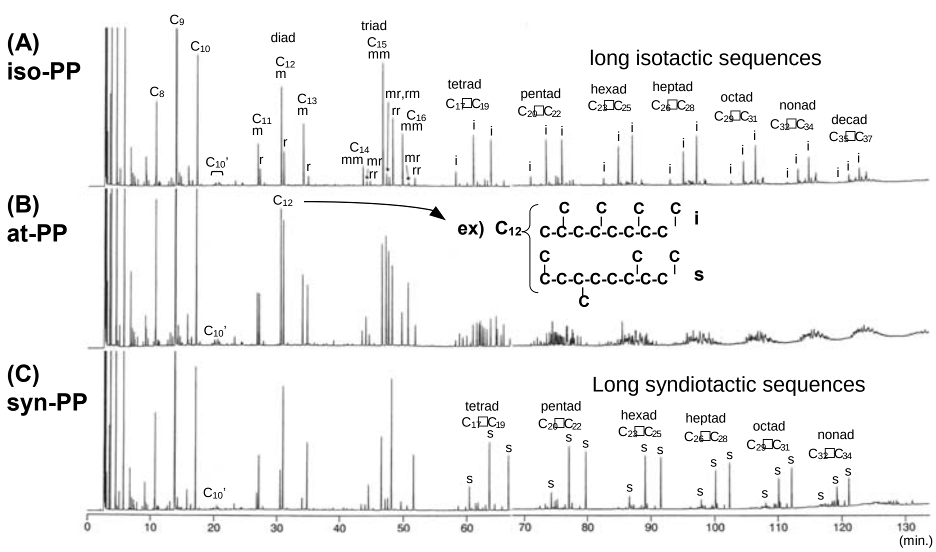
Propylene tetramers as pyrolysates reflecting meso-sequence

Pyrolysis-in-line Hydrogenation GC System



Typical Pyrograms of PPs

(by FID)

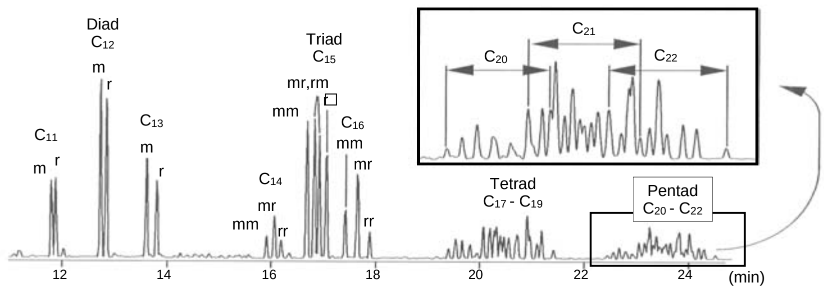


i: isotactic, s: syndiotactic

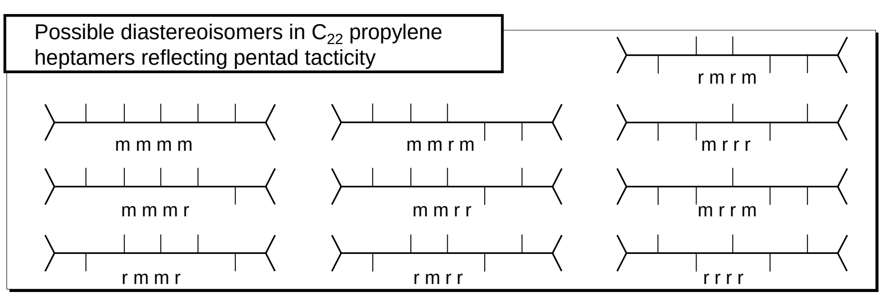
Diad and Triad Tacticity of PP samples

PP sample	by Py-GC (C_{13})		by ^{13}C-NMR		by Py-GC (C_{16})			by ^{13}C-NMR		
	% m	% r	% m	%r	%mm	%mr	%rr	%mm	%mr	%rr
ML-iso-PP_1	74.3	25.7	84	16	58.9	30.0	11.1	70	28	2
ML-iso-PP_2	84.6	15.4	96	4	79.6	7.5	13.0	94	4	2
ML-at-PP	55.8	44.2	57	43	27.7	54.3	18.0	30	53	17
ML-syn-PP	15.0	85.0	2	98	12.2	8.5	79.4	1	3	96
ZN-iso-PP	86.8	13.2	99	1	82.0	5.4	12.6	99	1	0
ZN-at-PP	49.0	51.0			33.2	34.4	32.5			
ZN-syn-PP	28.5	71.5	27	73	23.4	12.8	63.8	17	18	65

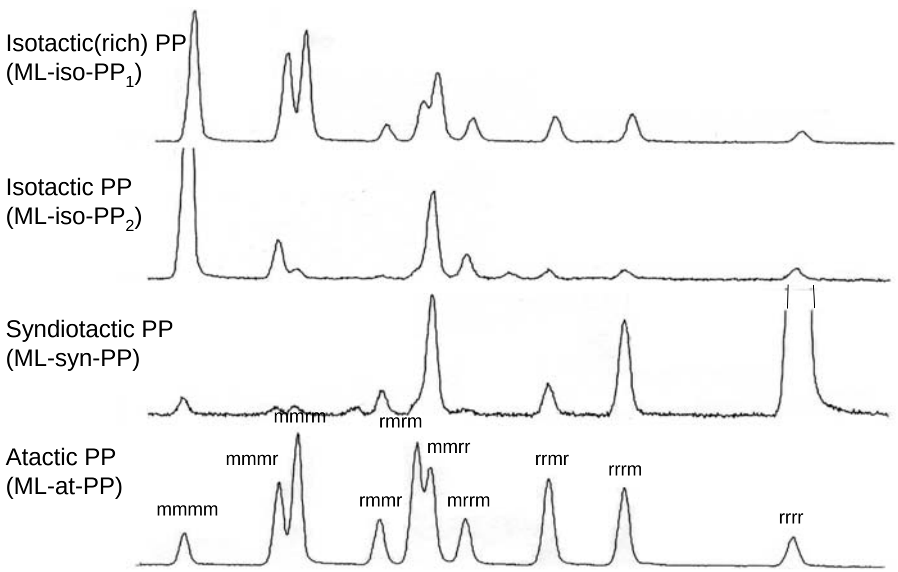
Diastereomeric Pyrolysis Products Reflecting Original Tacticity



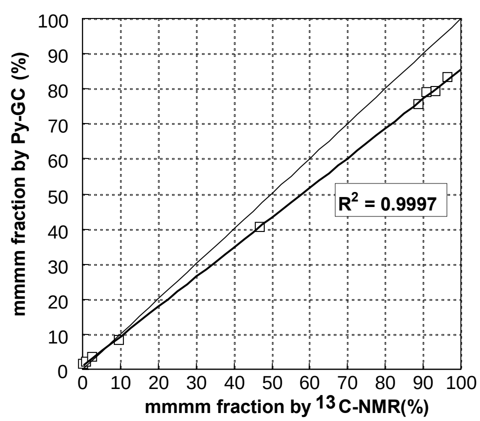
at-PP synthesized with a metallocene catalyst.



Single Ion Monitoring at m/z 310 Corresponding to C_{22} Products



Isotactic Pentad Tacticity (mmmm) in PP Determined by Py-GC



	ML-S_1	ML-S_2	ML-S_3	ML-A	ML-I_0	ML-I_1	ML-I_2	ZN-I_1	ZN-I_2
Py-GC	1.5	2.0	3.5	8.3	40.4	75.5	79.1	78.9	83.2
Py-GC with calibration	0.7	1.3	3.1	8.8	46.7	88.1	92.4	92.2	97.2
^{13}C-NMR	0.2	1.1	2.7	9.8	47	88.8	93.3	91	96.6

Chain end structures of polymers

Why chain end characterization is so important ?

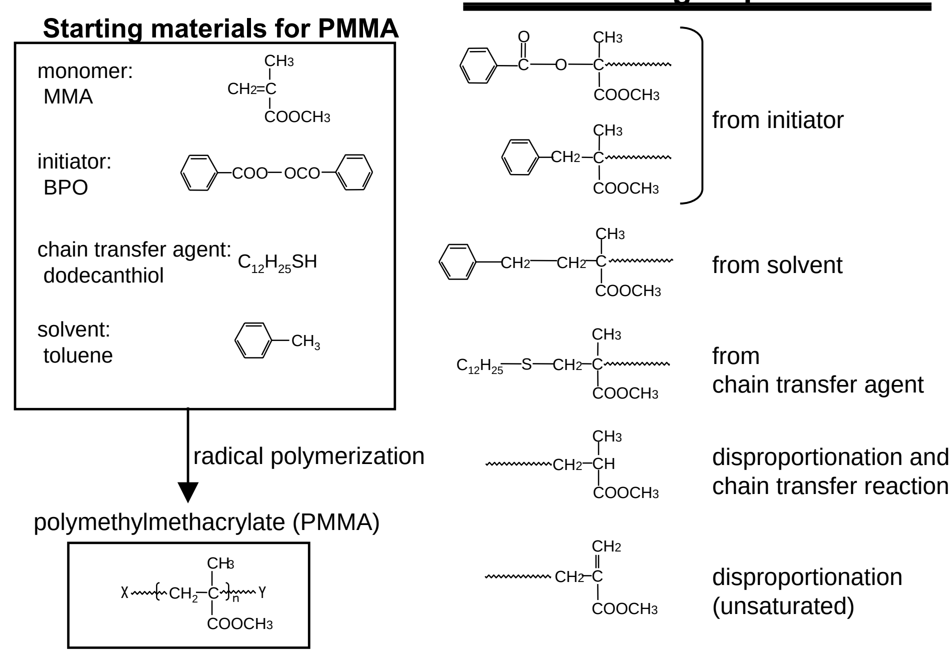
(A) The properties of various polymeric materials are often affected by the end groups even for the same kind:
thermal stability, transparency, coloration during injection and/or weathering,mechanical strength,etc.

(B) The characterization of chain end group are indispensable to understand the associated polymerization mechanisms:
initiation, propagation, chain-transfer, and termination reactions, etc.
since the chain end groups are keeping their most important history.

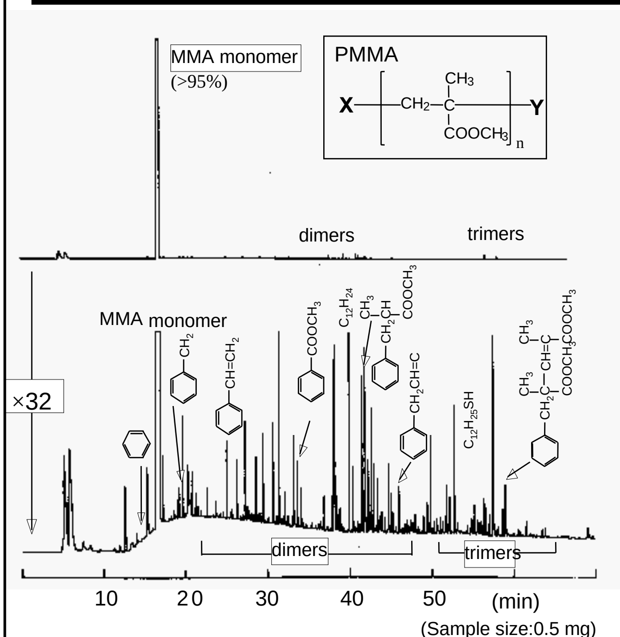
(C) Quantitative information of the end groups enable us to estimate exact M_n values for the given polymer system:

(D) More practically, many polymer industries are legally investigating the chain end groups in the polymeric materials of interest supplied from rival industries("survival spy").

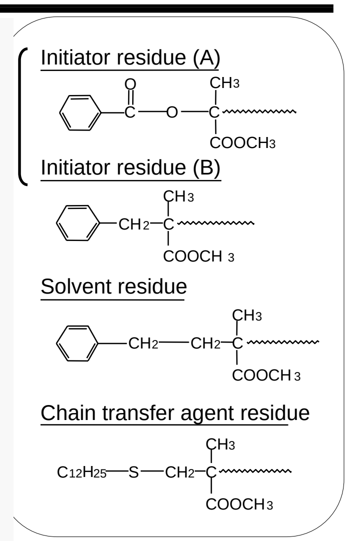
Possible end groups in PMMA



Pyrogram of radically polymerized PMMA at 460˚C

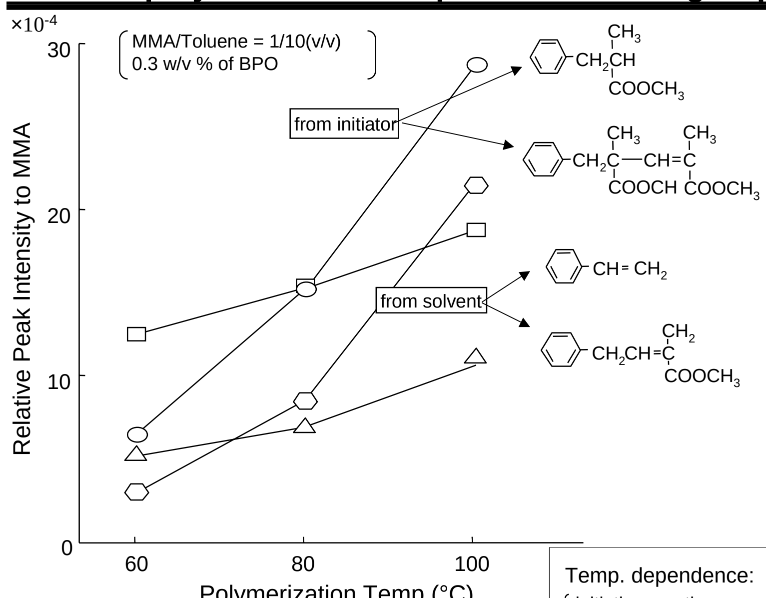


[*Polym. J.*, 21, 41-48 (1989)]



Initiator: BOP
Chain Transfer agent: dodecanethiol
Mn: 28,000

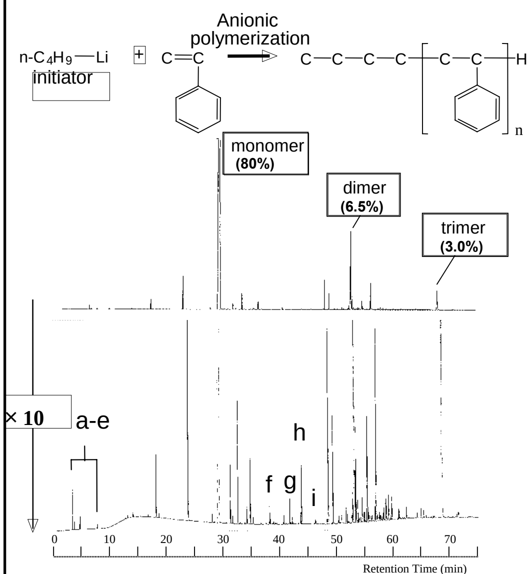
Effect of polymerization temperature on end group formation



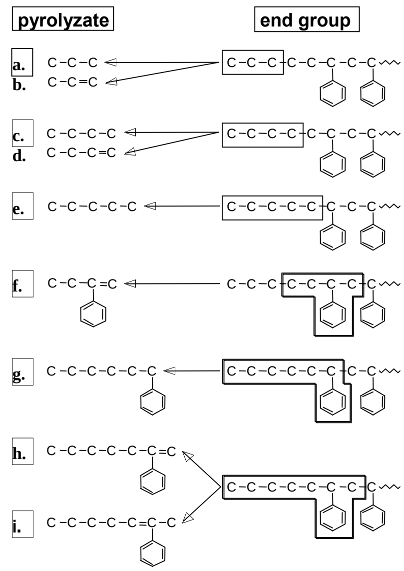
Yield(%) 0.1 7.3 22.3

Temp. dependence:
- initiation reaction > propagation reaction
- initiation reaction >chain transfer reaction to solvent

End Group Characterization in Anionically Polymerized Polystyrene



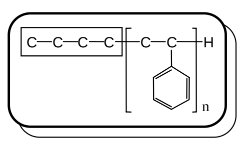
Pyrograms of anionically polymerized polystyrene (Mn = 9,000) at 600°C, sample size : 0.1mg



Formation of characteristic pyrolyzates of n-Bu end group in PS

[*J. Polym. Sci., Part-A*, 32, 383-388 (1994)]

Estimated Number-Average Molecular Weight of Anionically Polymerized PS

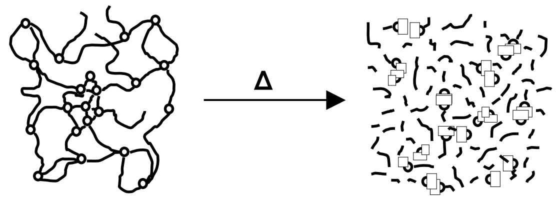


Sample	$\overline{M_n}$ by GPC/SEC	$\overline{M_n}$ by Py-GC
A	1,190	1,240
B	3,090	3,250
C	9,000	9,100
D	27,600	28,200
E	64,600	61,400
F	152,000	130,000
G	419,000	587,000
H	979,000	1,090,000

[*J. Polym. Sci., Part-A*, 32, 383-388 (1994)]
[*Macromolecules*, 30, 2542-2545 (1997)]

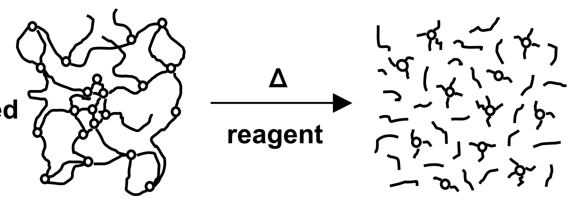
Characterization of Network Structure in Crosslinked Polymers

Ordinary Pyrolysis



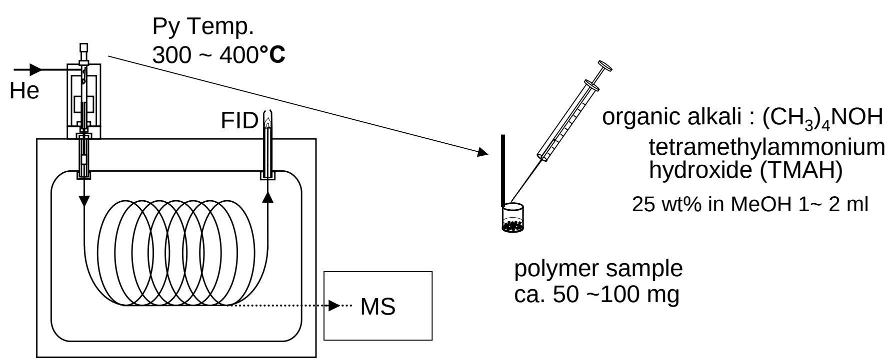
Too much fragmentation

Thermally-assisted Chemolysis



Selective decomposition with preserving cross-linking points

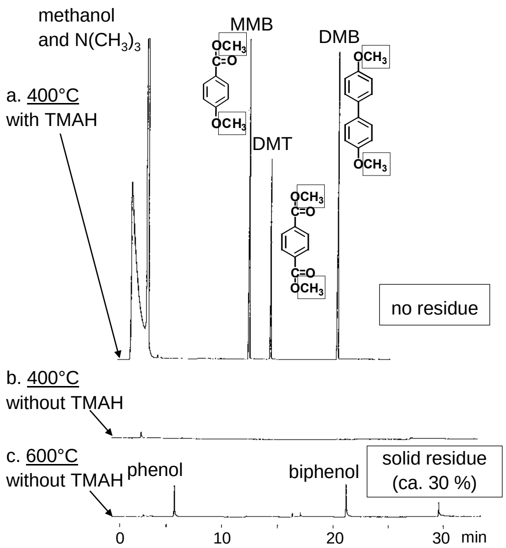
Thermally Assisted Hydrolysis and Methylation GC of Condensation Polymers

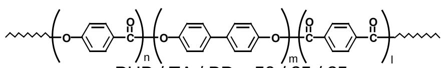


$$R_1-\overset{O}{\overset{\|}{C}}-O-R_2 \xrightarrow[\Delta]{(CH_3)_4NOH} R_1-\overset{O}{\overset{\|}{C}}-O-CH_3 + H_3C-O-R_2$$

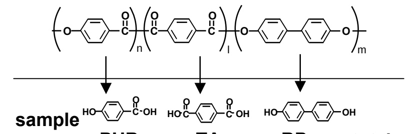
$$R_3-O-\overset{O}{\overset{\|}{C}}-O-R_4 \xrightarrow[\Delta]{(CH_3)_4NOH} R_3-O-CH_3 + H_3C-O-R_4 + CO_2$$

Compositional Analysis of fully Aromatic Polyester





PHB / TA / BP = 50 / 25 / 25
Sample size: 0.05 mg



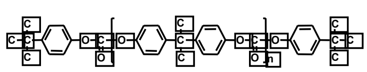
sample	PHB	TA	BP	total
A	85.7 (84.6)	7.0 (7.7)	7.3 (7.7)	100
B	67.9 (66.7)	15.1 (16.7)	17.0 (16.7)	100
C	50.5 (50)	24.0 (25)	25.5 (25)	100
D	34.1 (33.3)	32.0 (33.3)	33.9 (33.3)	100

( ) : feed composition

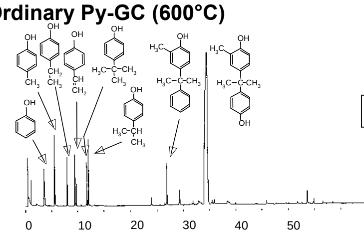
reproducibilities : CV < 1.0 %

[*J. High Res. Chromatogr*., 14, 388-391 (1991)]
[*J. Anal. Appl. Pyrolysis,* 33, 167-1480 (1995)]

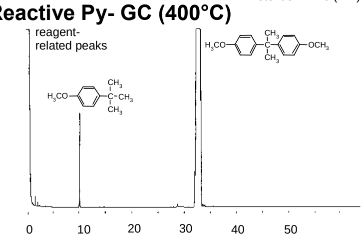
End group determination of solvent method polycarbonate



Ordinary Py-GC (600°C)



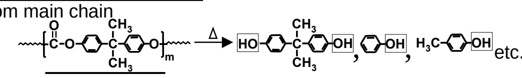
Reactive Py- GC (400°C)



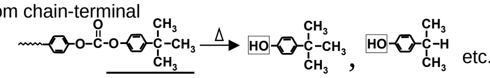
[*Polym. J.*, 28, 1090-1095 (1996)]

Conventional pyrolysis

from main chain

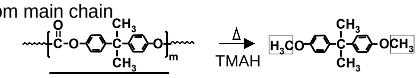


from chain-terminal

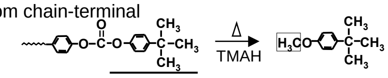


Reactive pyrolysis in the presence of TMAH

from main chain



from chain-terminal



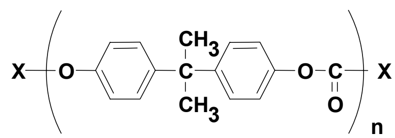
Determination of M_n

Fraction No.	Estimated Mn values by SEC	by Py-GC*	by ^{1}H-MNR
S-1	23,400	26,900	30,200
S-2	8,300	9,500	9,600
S-3	4,000	4,700	--

* :CV values: 0.5~2%

Abnormal structures in polycarbonate (PC)

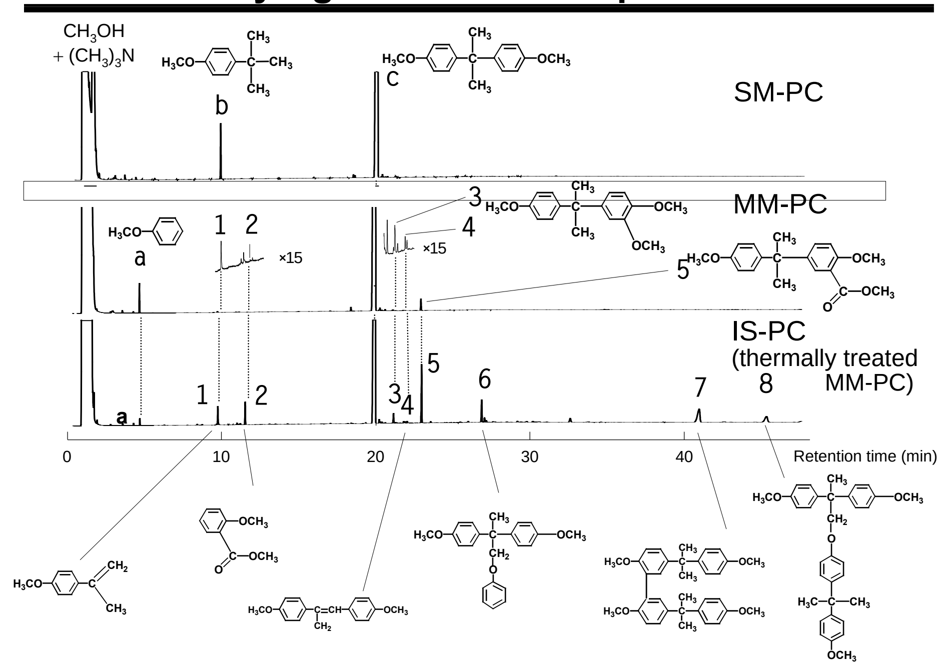
[*Macromolecules*, 33, 8173-8183(2000); *Polym. Degrad. Stab.*, 74, 171-176(2001)]



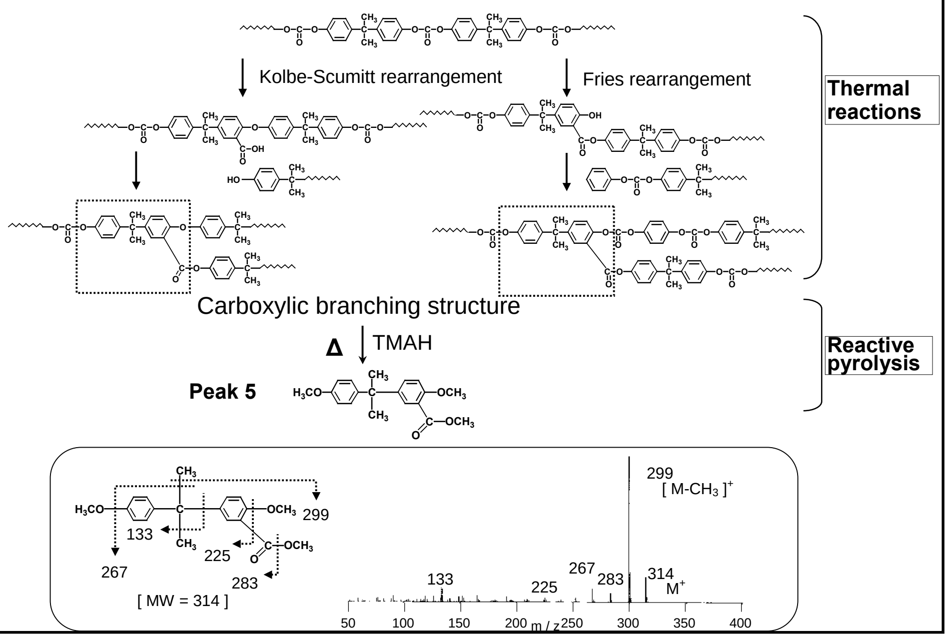
PC samples

Sample name	Preparation method	Degree of branching and/or cross-linking structures	
SM-PC	Solution method	Low	industrial PC
MM-PC	Melt method	Somewhat	industrial PC
IS-PC	Thermal□ insolubilization with MM-PC (at 300°C in air for 3 hours)	considerable	

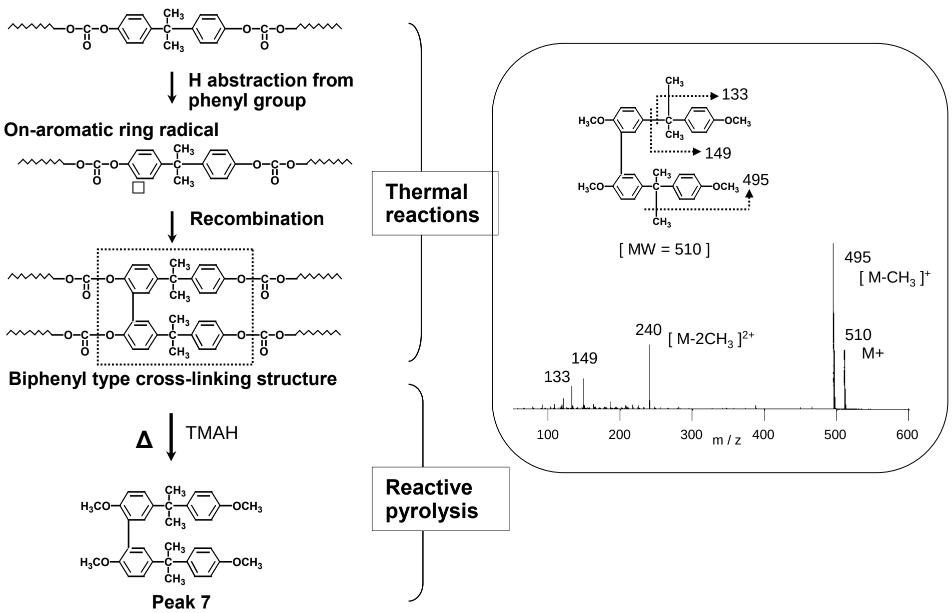
Pyrograms of PC samples



Formation pathway of the carboxylic branching structure and its characteristic product (peak 5)

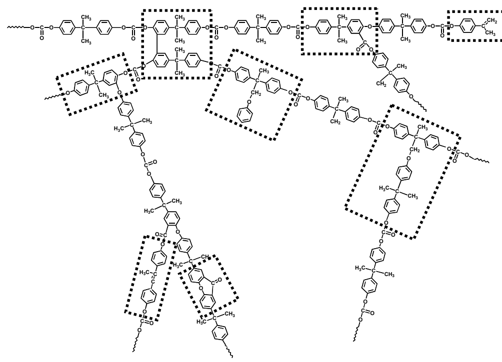


Formation pathway of the biphenyl type cross-linking structure and its characteristic product (peak 7)



Various abnormal structures such as the branching, cross-linking and xanthone structures in thermally treated PC samples were confirmed by Py-GC in the presence of TMAH.

Furthermore, it was proved that some of these structures would be formed in the industrial polymerization reactor to synthesize the PC by the melt method.



Possible structures of the thermally treated PC

Characterization of network structure in UV-cured resins

UV-curable resins

Characteristics : rapid curing
low temperature curing
solventless

Versatile utilization : coatings, ink binders, photoresists, dental materials etc.

properties ⇔ **structures**
close correlation

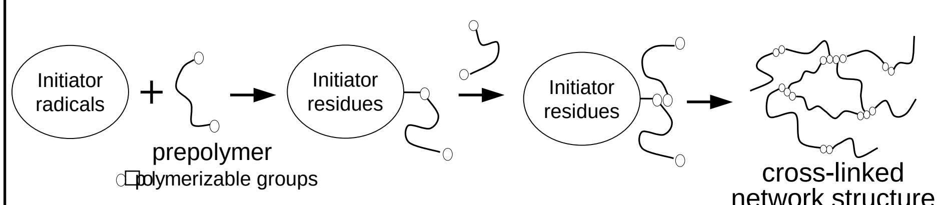
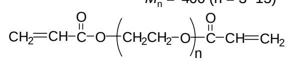


Photo-cured resin samples

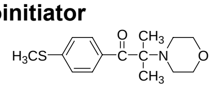
Prepolymer

M_n = 400 (n = 3~15)



polyethyleneglycol diacrylate

Photoinitiator



IRGACURE907

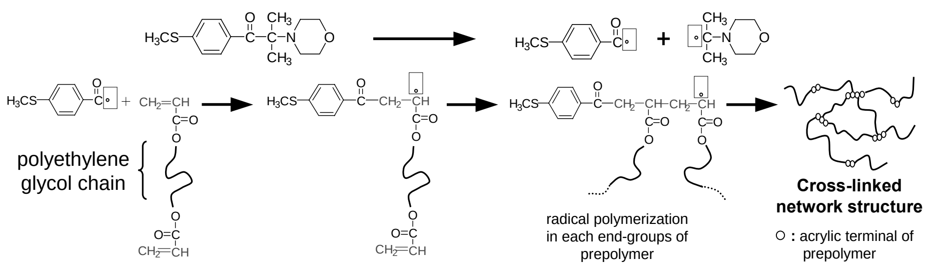
Photo-curable resin mixtures

prepolymer / photoinitiator = 100 / 3 (wt)

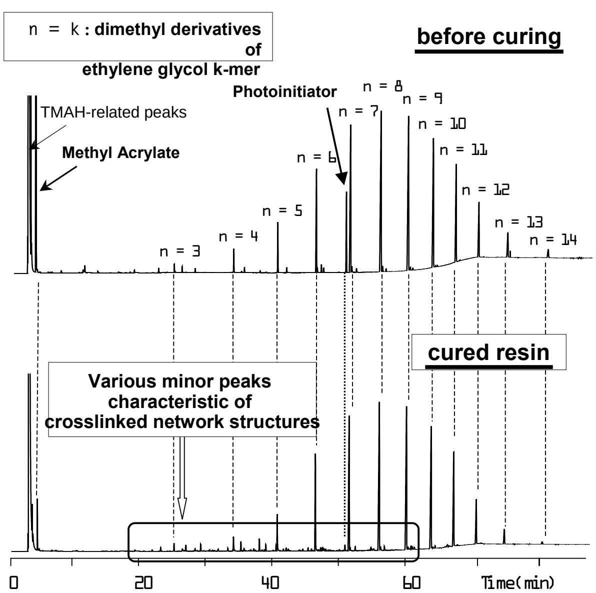
Light source□ 80 W/cm medium pressure mercury lamp (**365** nm)
Irradiation□□225 mJ/cm^2 in air

Photo-cured resin samples

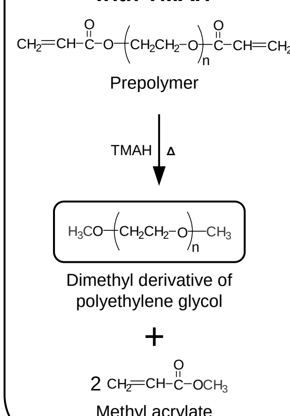
Photo-curing Reaction



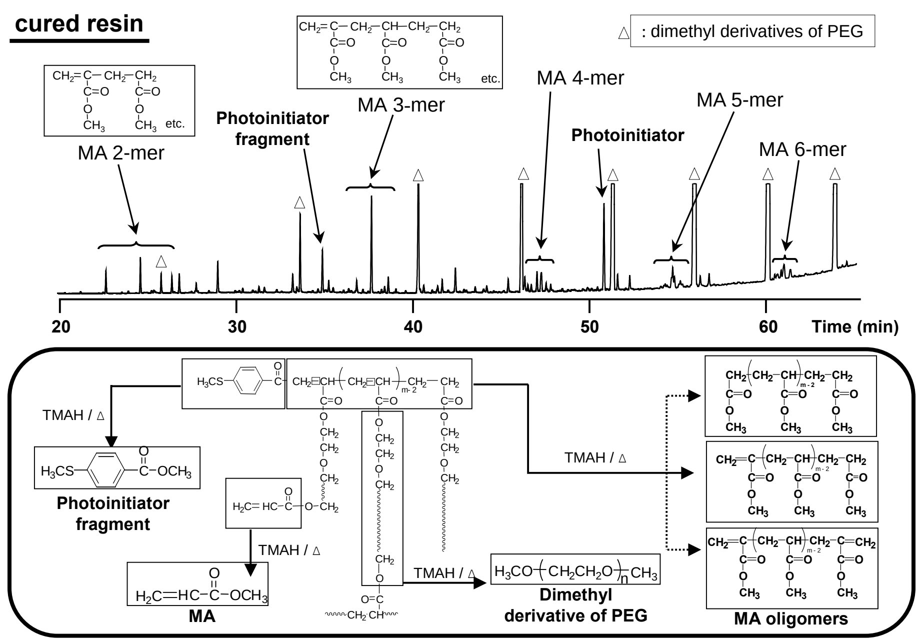
Pyrograms of UV-curable resin before and after irradiation



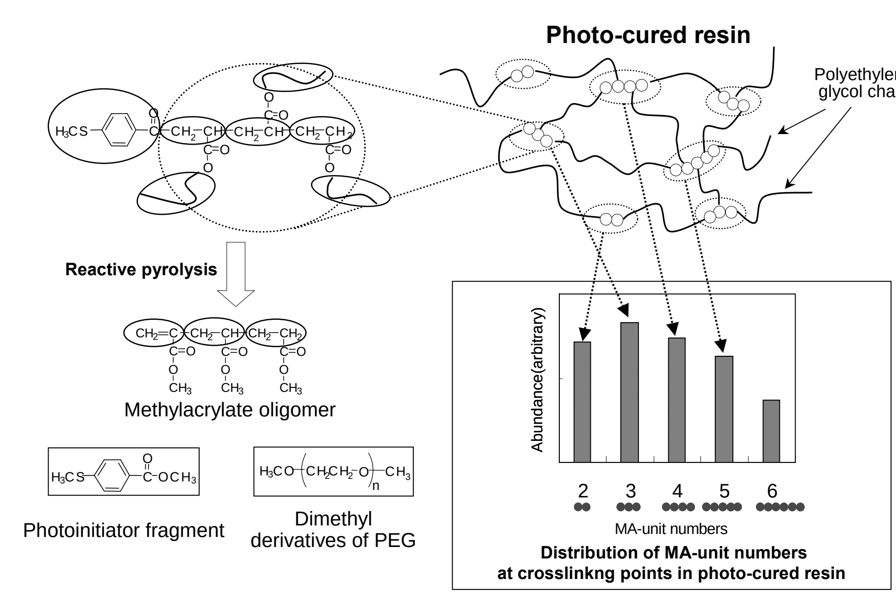
The selective chemolysis at the ester linkage achieved by pyrolysis with TMAH



Peaks reflecting cross-linked network structures of cured resin



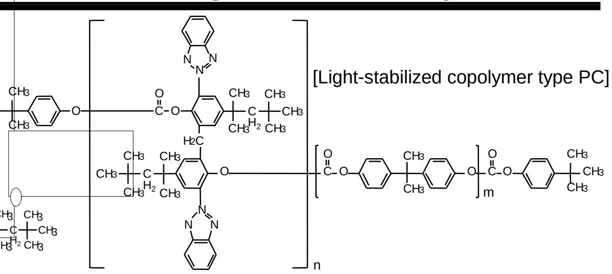
Cross-linked network structures of UV-cured resin

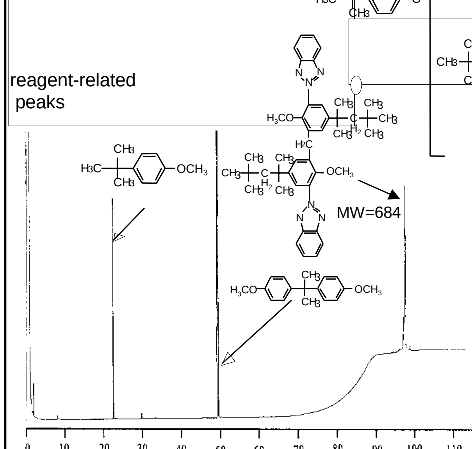


Molecular properties of polymeric materials and their characterization techniques

Molecular property	Characterization techniques
A: Purity Residual solvent, catalyst, monomer etc.	Chemical analysis, Various chromatography (GC, TLC, HPLC etc.) Mass spectrometry (MS), Spectroscopic methods (IR, NMR etc.), Emission analysis, Atomic Absorption etc.
B: Average molecular weight (MW) and MW distribution Number average MW (Mn), Weight average MW (Mw), Viscosity average MW (Mh), Z average MW (Mz), MW distribution, Polydispersity (MwMn)etc.	Membrane osmometry, Vapor pressure osmometry, Ebullioscopy, Light scattering, Ultra centrifugation, Viscometry, Size exclusion chromatography (SEC), (MALDI-)MS,NMR,Pyrolysis-GC/MS (Py-GC/MS) etc.
C: Microstructure a. Branching	
Short chain branching	IR, NMR, Py-GC/MS etc.
Long chain branching	NMR, Solution theory
b. Stereoregularity Average Stereoregularity,Stereoregular distribution, Stereoregular sequence distribution etc.	IR, NMR, TLC, Py-GC/MS etc
c. Bonding structure Regioirregularity,1,4- or 1,2-linkage,cis-or trance-etc.	IR, NMR, Py-GC/MS, Chemorysis-GC/HPLC etc.
d. End group	IR, NMR, Py-GC/MS, MALDI-MS, Titration etc.
D: Chemical structure of copolymers a. Average chemical composition	Elemental analysis, Chemical analysis, IR, NMR, Py-GC/MS, Chemorysis-GC/HPLC etc.
b. Distribution in chemical composition	Cross-fractionation, TLC, TREF, SEC, HPLC, LC-NMR, MALDI-MSetc
c. Sequence structure Run number, Average sequence length, Sequence distribution	IR, NMR, Py-GC/MS, Chemorysis-GC, MALDI-MS
E: Microgel□Crosslinking structure a. Weight fraction of gel	Filtration, Ultra-Centrifigation
b. Network structure of insolube crosslinking polymer	Py-GC/MS, Elemental Analysis, IR, Thermal Analysis, Swelling measurements etc.

Simultaneous determination of copolymer composition and average molecular weight of PC copolymer





Composition and M_n of fractionated PC copolymer

Sample	Compositions (mol%) BPA unit	Benzotriazole-type monomer unit	total	M_n
F-1	71.0	29.0	100	4.31×10^3
F-2	88.1	11.9	100	4.56×10^3
F-3	91.8	8.2	100	6.59×10^3
F-4	94.6	5.4	100	10.4×10^3

Pyrogram of light stabilized PC at 400°C in the presence of TMAH

[*J. Anal. Appl. Pyrolysis,* 40, 321-329 (1997)]