The Abdus Salam
International Centre for Theoretical Physics

United Nations
Educational, Scientific and
Cultural Organization

IAEA
International Atomic Energy Agency

2227-6

Joint ICTP-IAEA Workshop on Radiation Resistant Polymers

14 - 18 March 2011

STABILIZATION OF POLYPROPYLENE FOR RADIATION STERILIZATION

Olgun Güven
Hacettepe University
Ankara
Turkey

STABILIZATION OF POLYPROPYLENE FOR RADIATION STERILIZATION

Olgun Güven

Hacettepe University
Department of Chemistry
Beytepe 06800, Ankara, TURKEY
www.polymer.hacettepe.edu.tr

Lecture given at the ICTP/IAEA Workshop on “Radiation Resistant Polymers”, 14-18 March 2011, Trieste, Italy

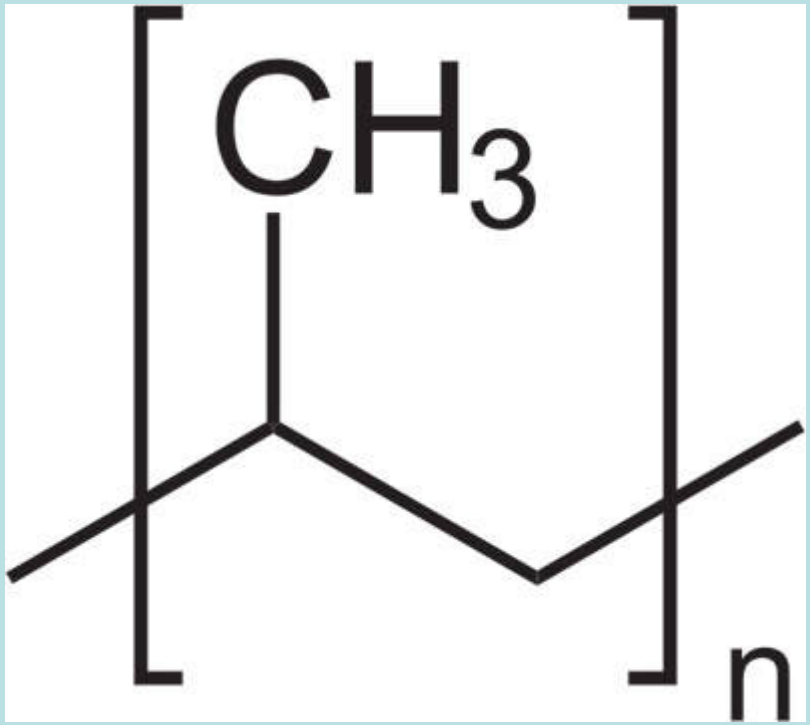
Materials used in disposable medical supplies

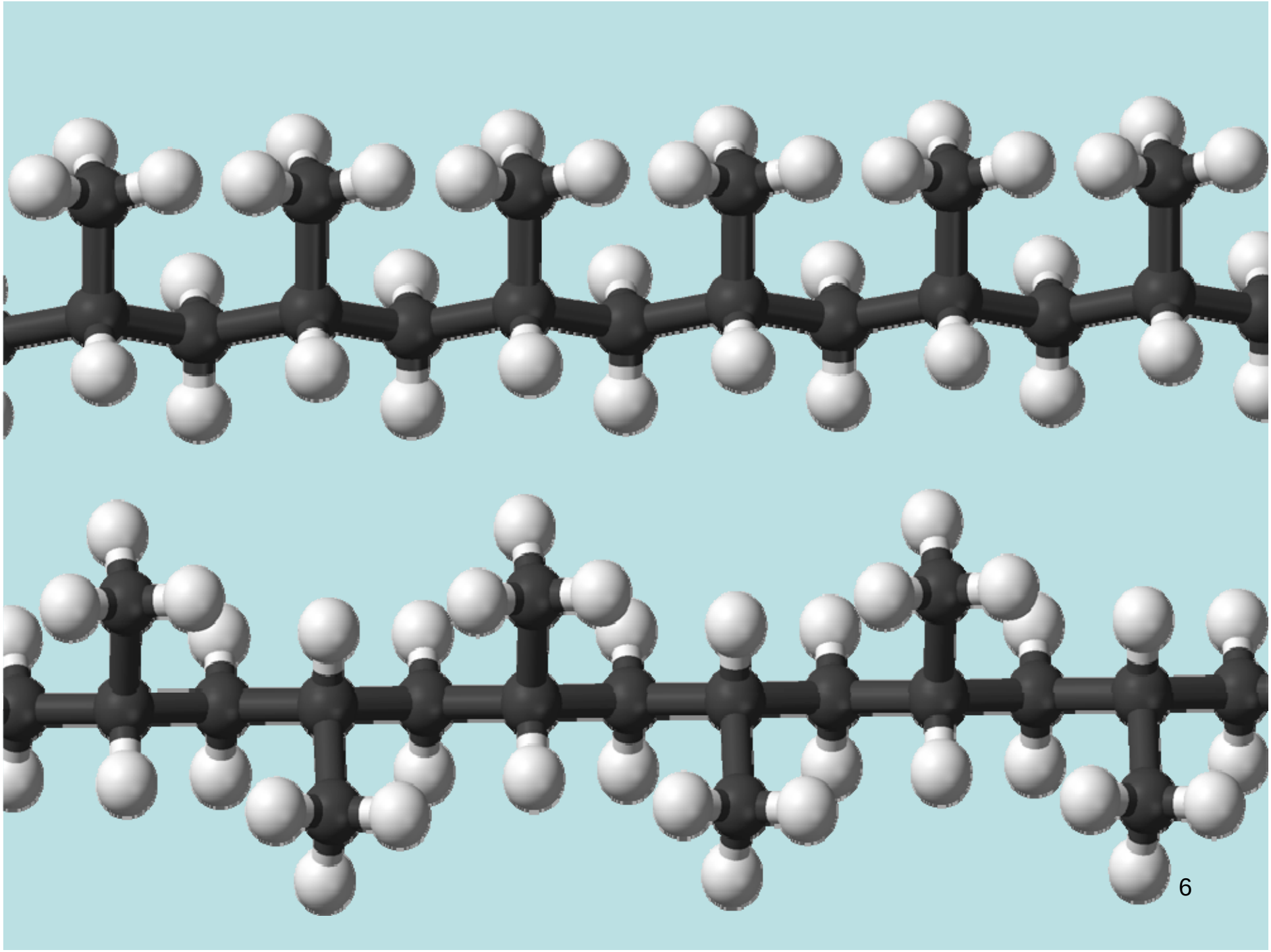
Medical Supplies	Materials
Syringes	Polypropylene, polystyrene, polyethylene, rubber, glass
Blood transfusion sets	Poly(vinylchloride), polypropylene, rubber, polyamides, polycarbonate,
Blood shunts	Poly(vinylchloride), polypropylene, polyamides
Nutrition tubes	Poly(vinylchloride), polypropylene, natural rubber
Dialyzers (artifical kidneys)	Polypropylene, poly(vinylchloride), polyethylene, polystyrene, polycarbonate, rubber,
Surgical sutures	Silk, collagen, polypropylene, polyamides, polyesters

PP: Material of Choice in Medical Use

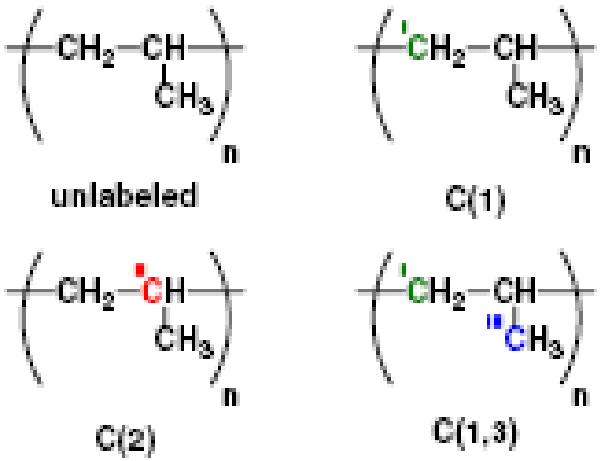
- Non-toxic
- Inert
- Low Cost
- Ease of extrusion, molding


1
2
3
4
5ml

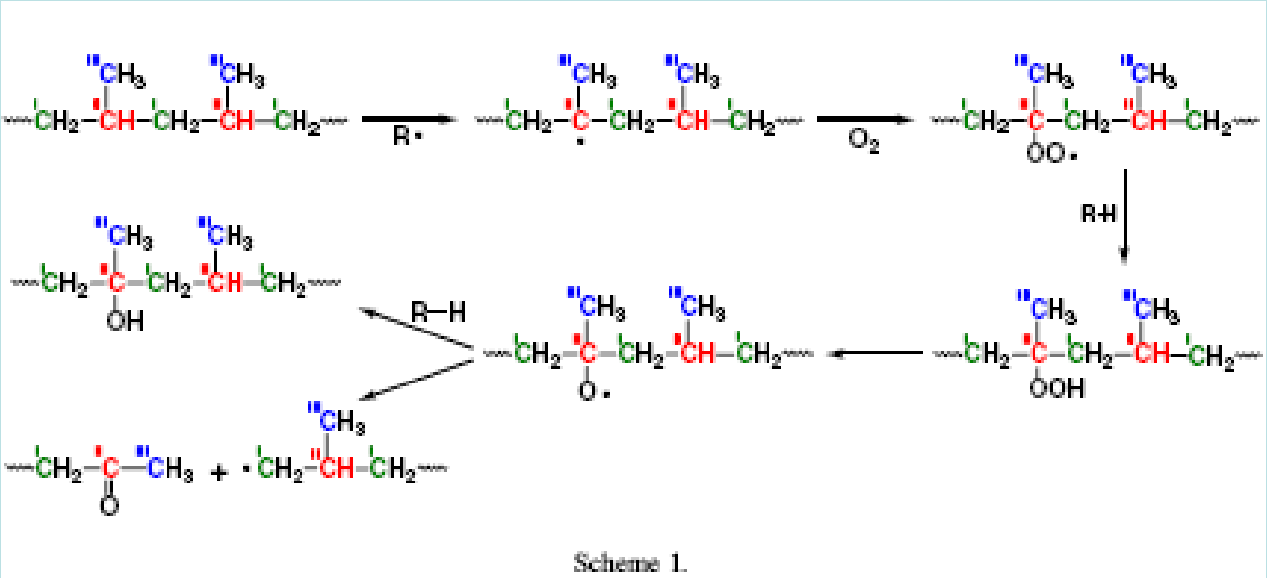

CH3
n



Labelling of PP

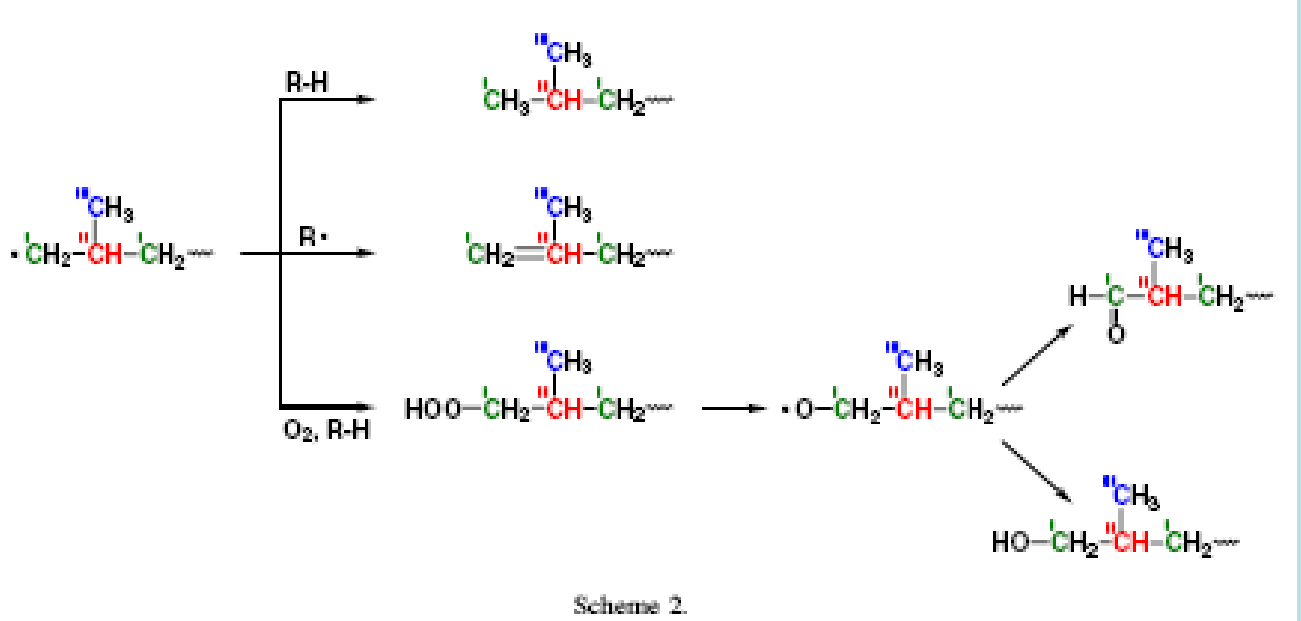


Radiochemical Changes in PP



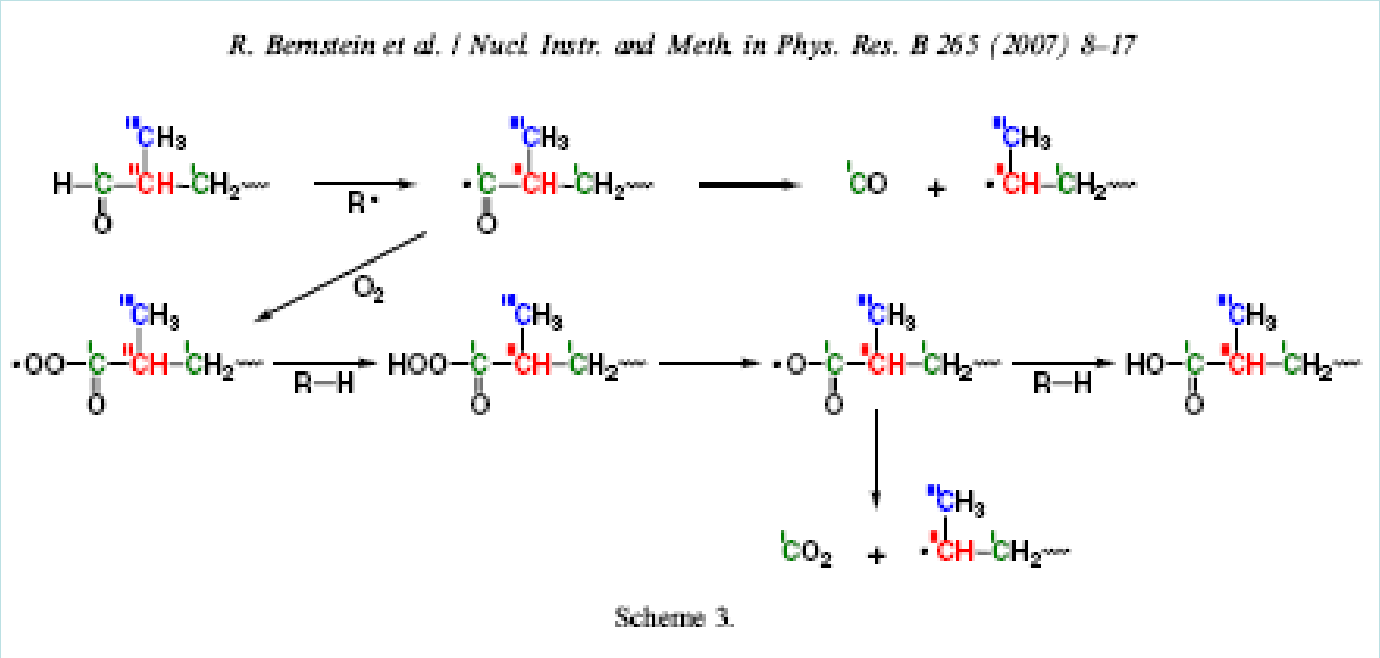
Scheme 1.

Radiochemical Changes in PP



Scheme 2.

Radiochemical Changes in PP



(1) $R \rightsquigarrow 2R\cdot$

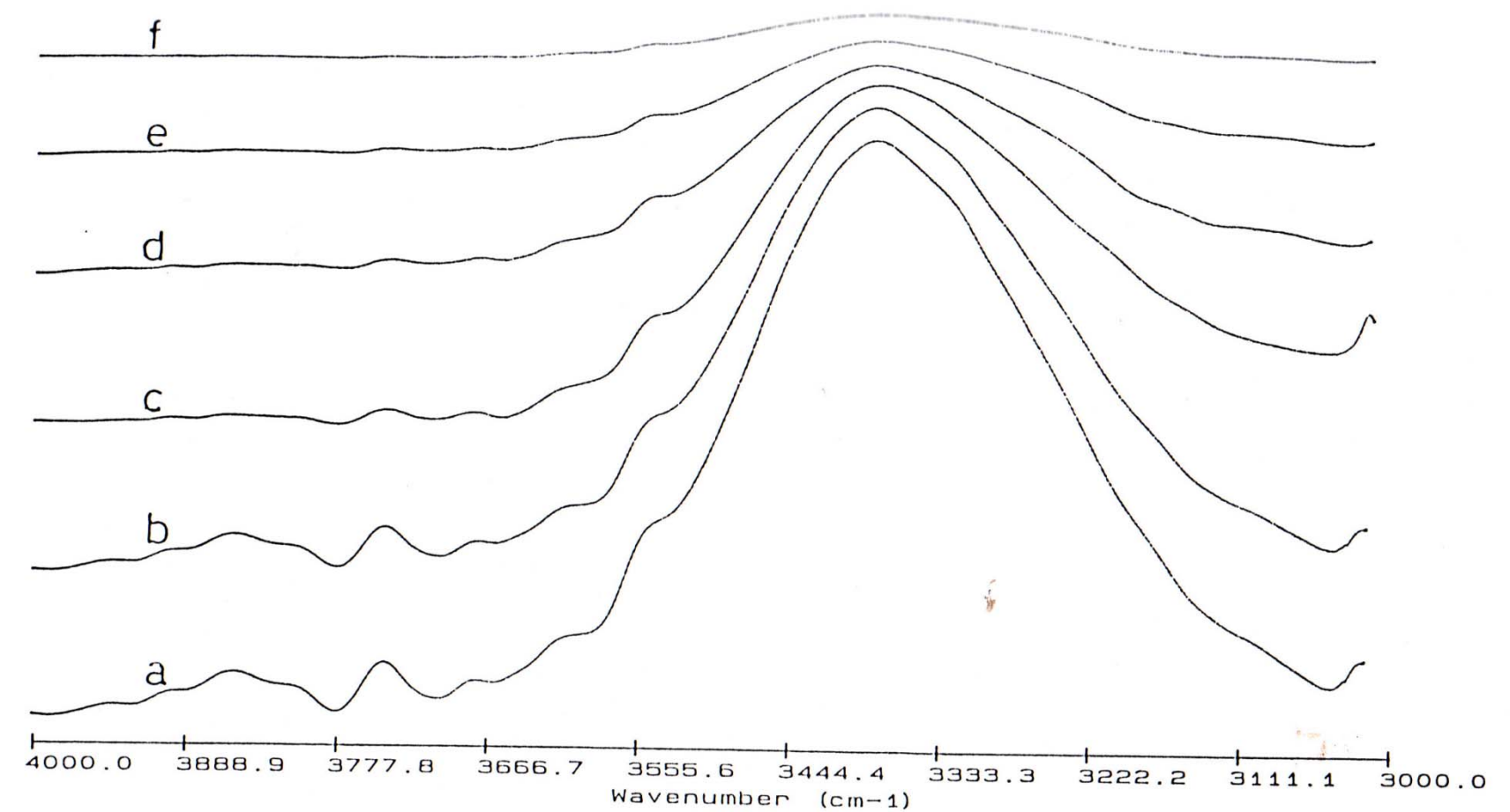
(2) $R\cdot + O_2 \rightarrow RO_2^{\cdot}$

(3) $RO_2^{\cdot} + RH \rightarrow ROOH + R\cdot$

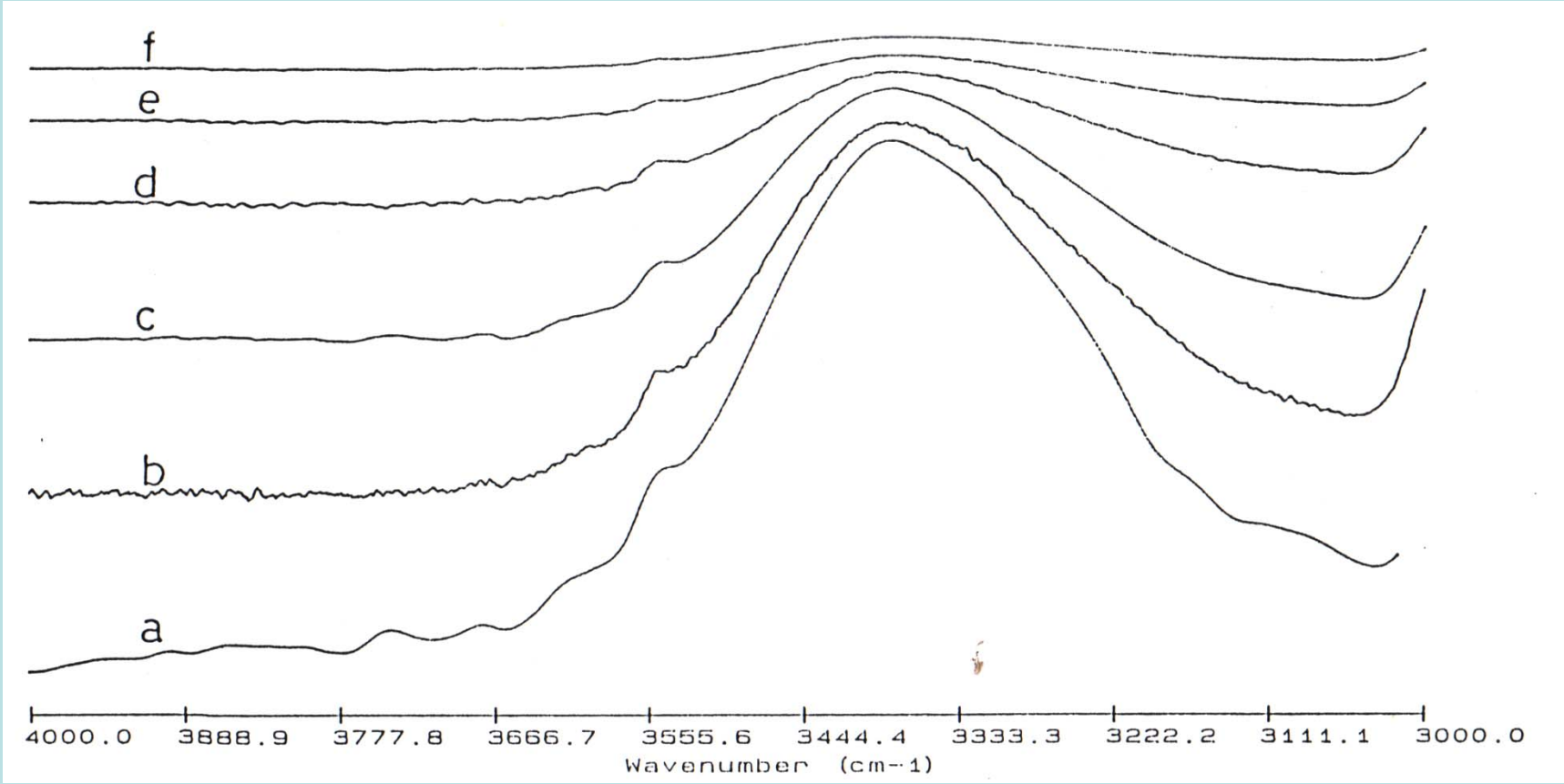
(4) $RO_2^{\cdot} + R\cdot \rightarrow ROOR$

(5) $RO_2^{\cdot} + RO_2^{\cdot} \rightarrow ROOR + O_2$

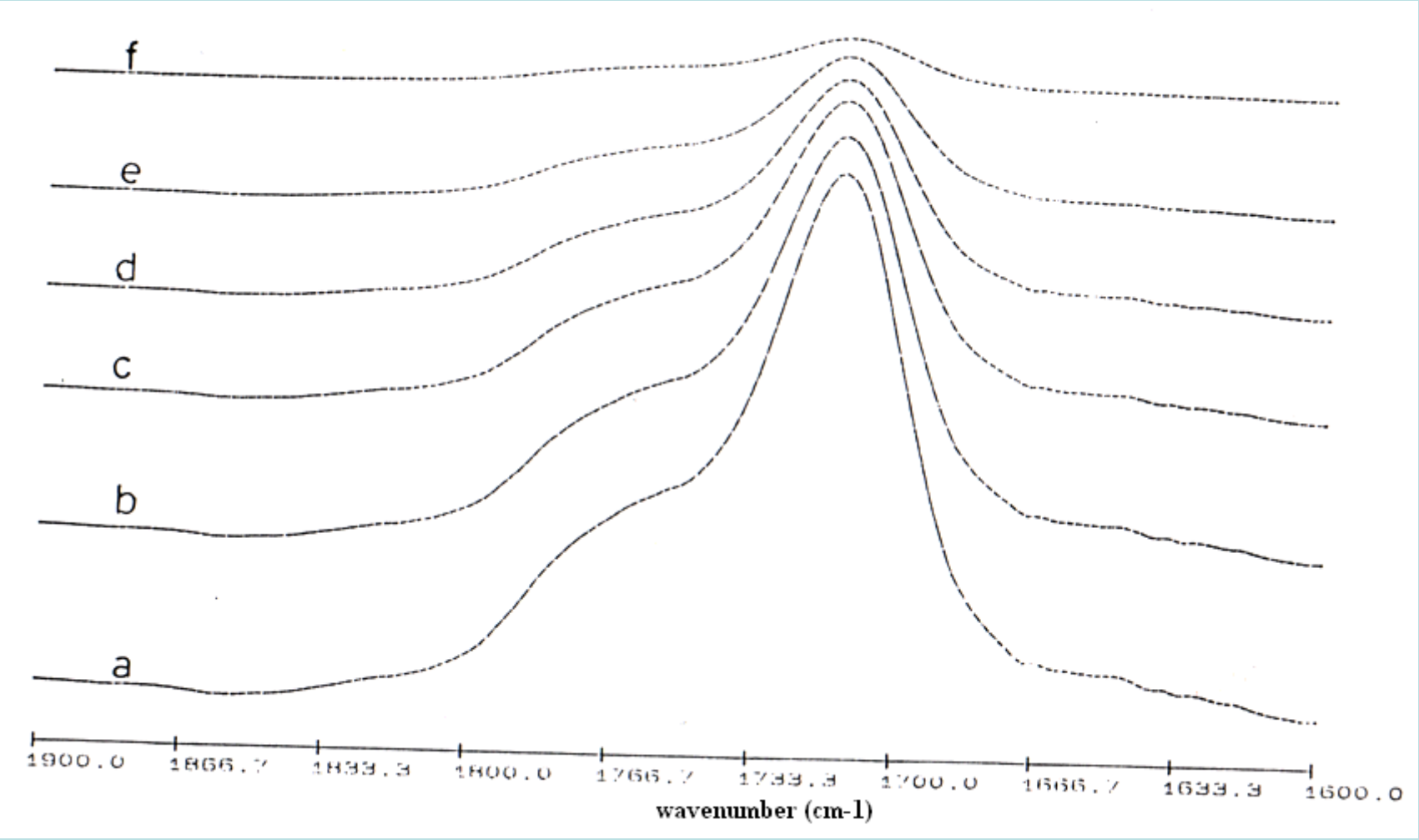
(6) $R\cdot + R\cdot \rightarrow R{-}R$



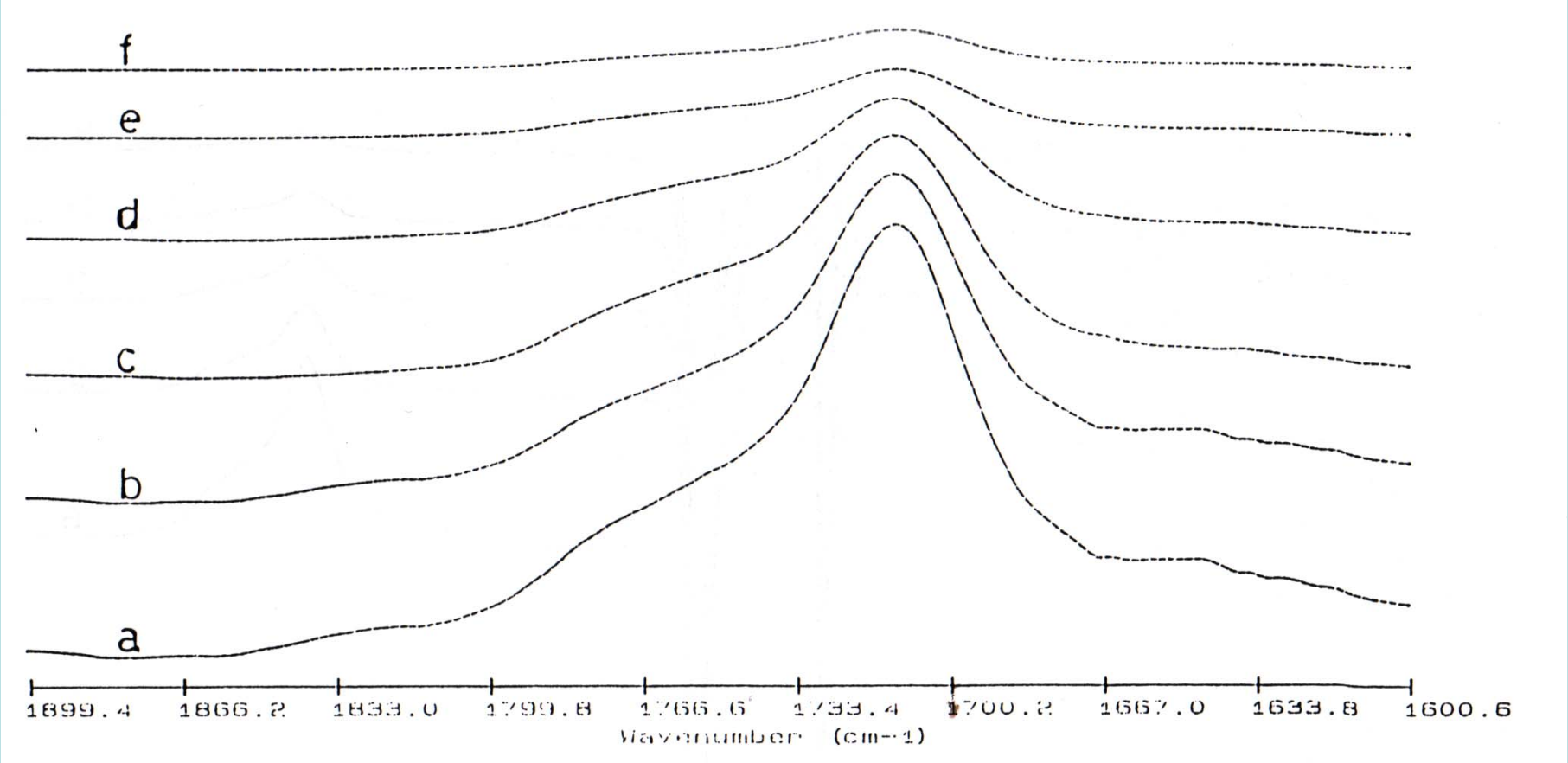
Difference spectra showing the absorbance of ROH and ROOH bands with cross sections from (a) outermost layer to (f) midsection



Difference spectra showing the absorbance of ROH and ROOH bands with cross sections from (a) innermost layer to (f) midsection



Difference spectra showing the absorbance of RCO and RCOOH bands with cross sections from (a) outermost layer to (f) midsection



Difference spectra showing the absorbance of RCO and RCOOH bands with cross sections from (a) innermost layer to (f) midsection

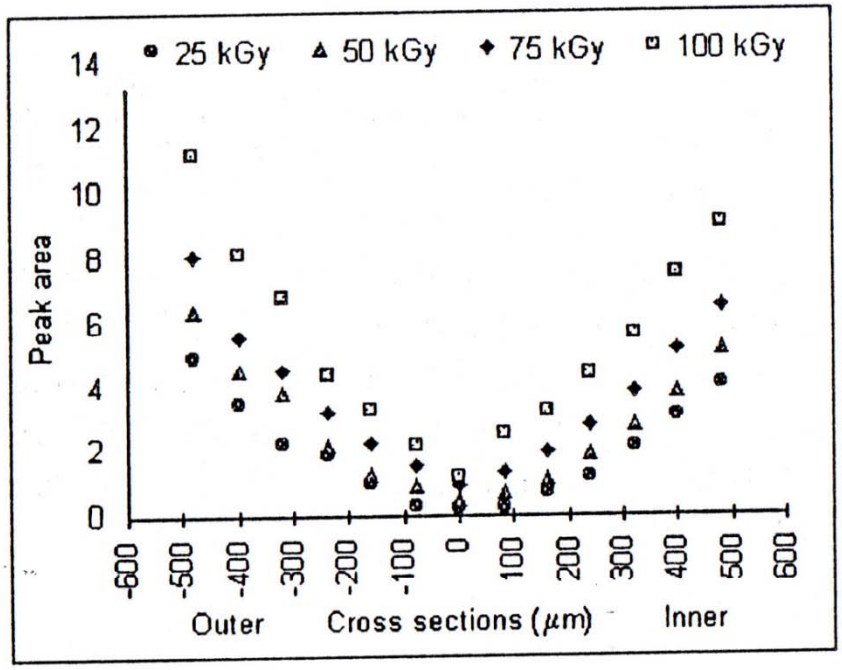


Figure. Changes of the peak area of OH band with cross section

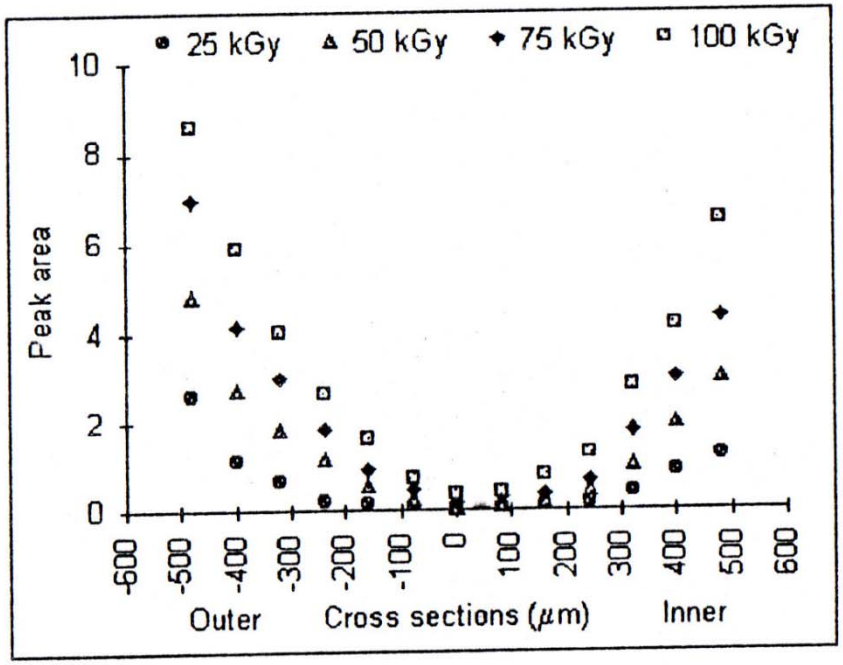
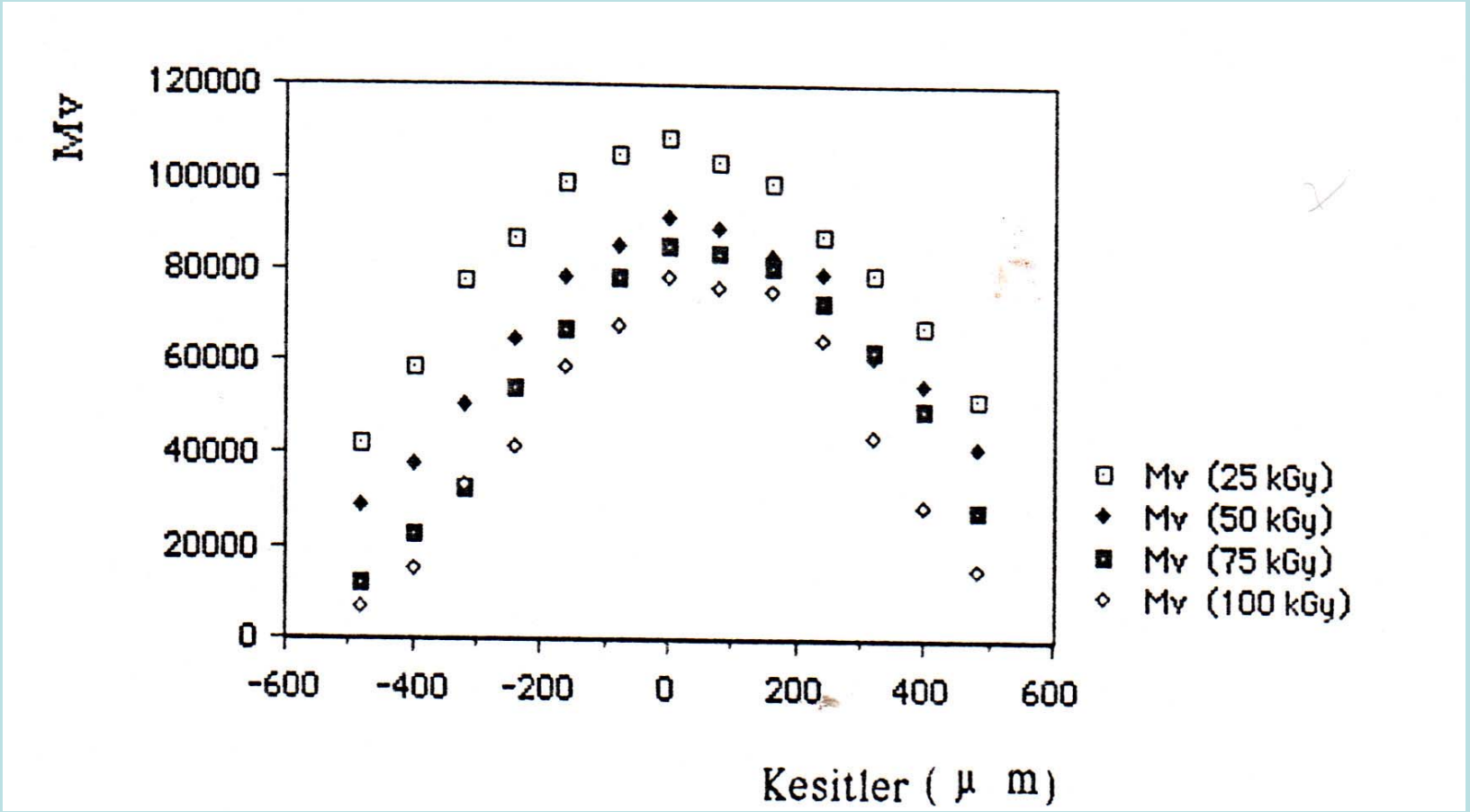
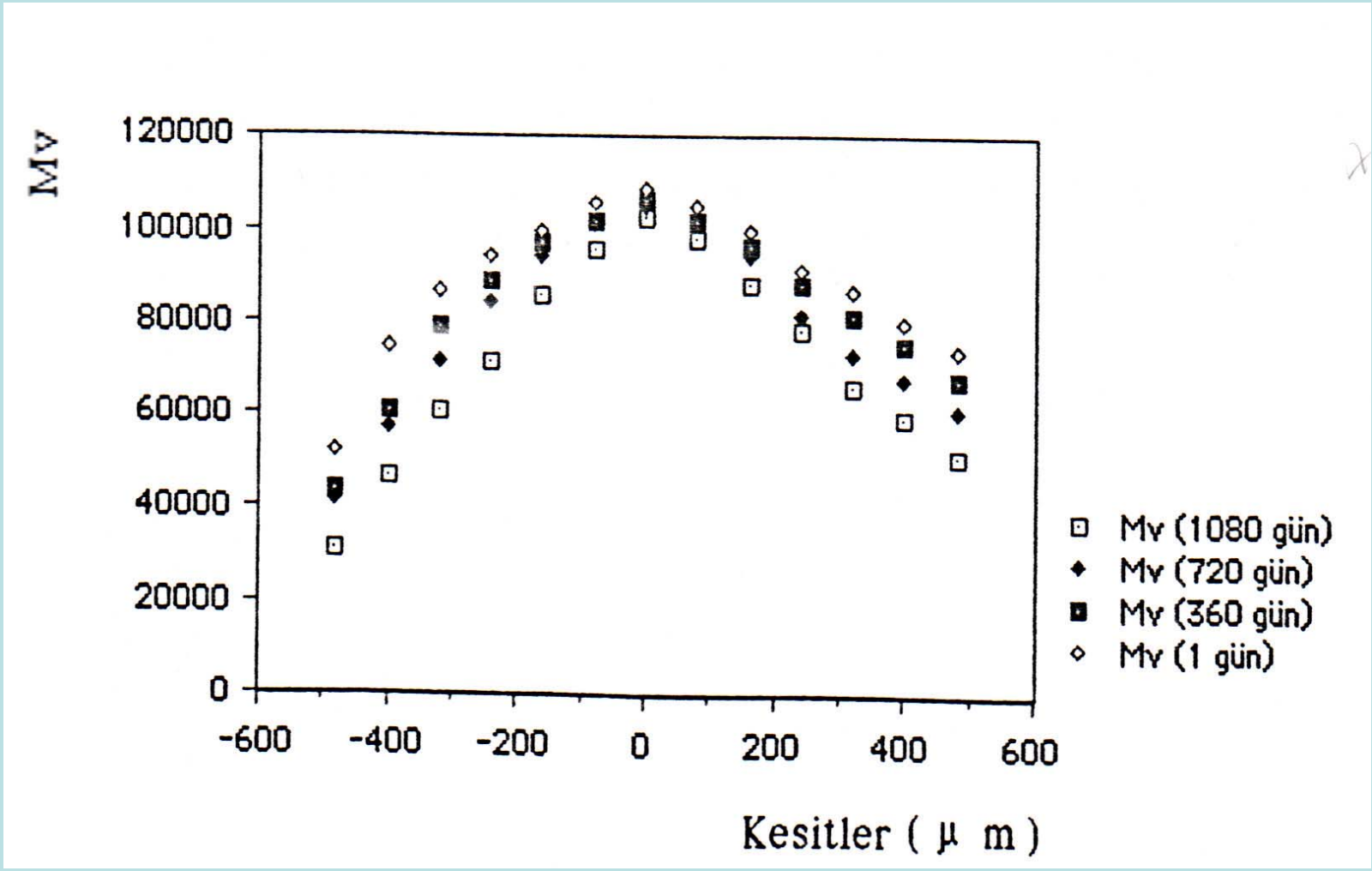


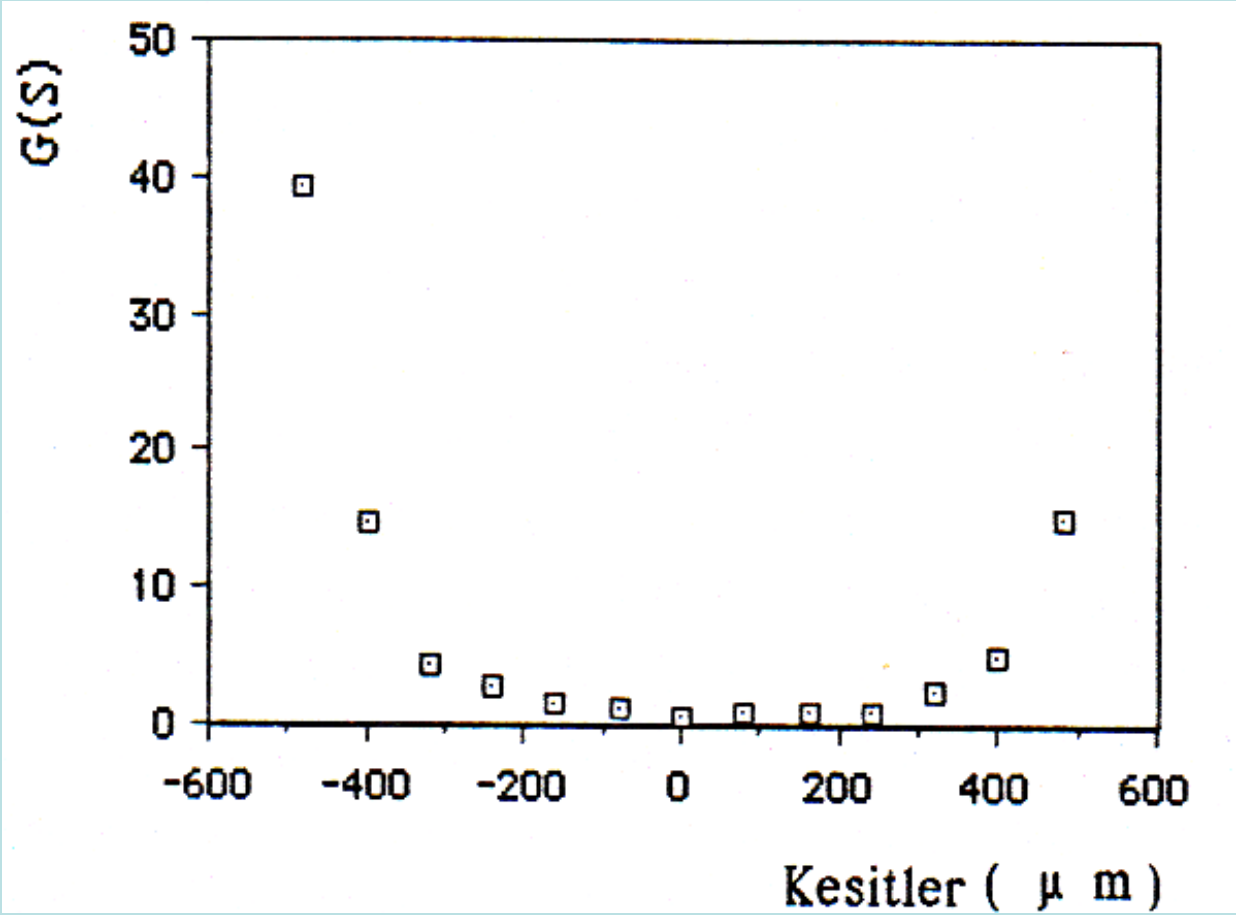
Figure. Changes of the peak area of C=O band with cross section



Changes in the viscosity average molecular weight of PP with cross section



Crosssectional change in the molecular weight of PP syringe irradiated to 25 kGy and aged under ambient conditions



Change in the G(S) value with the crosssection of PP syringe

Table. The changes in the G(OH), G(C=O), G(OH)+G(C=O) and G(S) values with depth of cross sections

Cross sections (μm)	G(OH)	G(C=O)	G(OH)+G(C=O)	G(S)
-480	5.80	34.8	40.6	39.4
-400	2.90	12.6	15.5	14.8
-320	0.80	3.80	4.60	4.26
-240	0.60	2.50	3.10	2.97
-160	0.19	1.60	1.79	1.68
-80	0.17	0.94	1.11	1.25
0	0.15	0.62	0.77	0.76
80	0.17	0.69	0.86	0.82
160	0.16	0.68	0.84	0.84
240	0.19	0.78	0.97	0.95
320	2.10	2.10	2.60	2.51
400	1.52	4.50	6.02	5.10
480	2.90	13.5	16.4	15.1

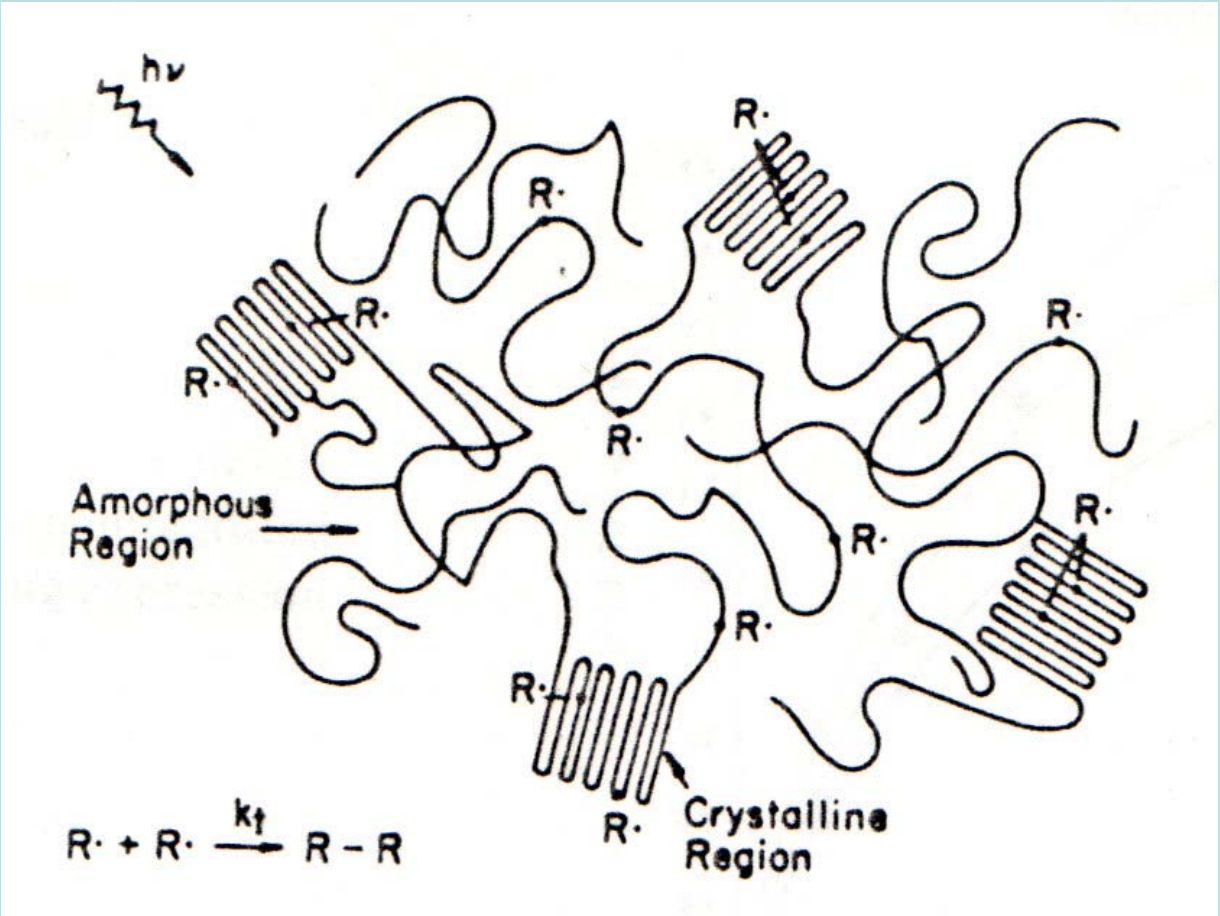


Figure. Schematic representation of radicals induced by γ-irradiation in isotactic polypropylene

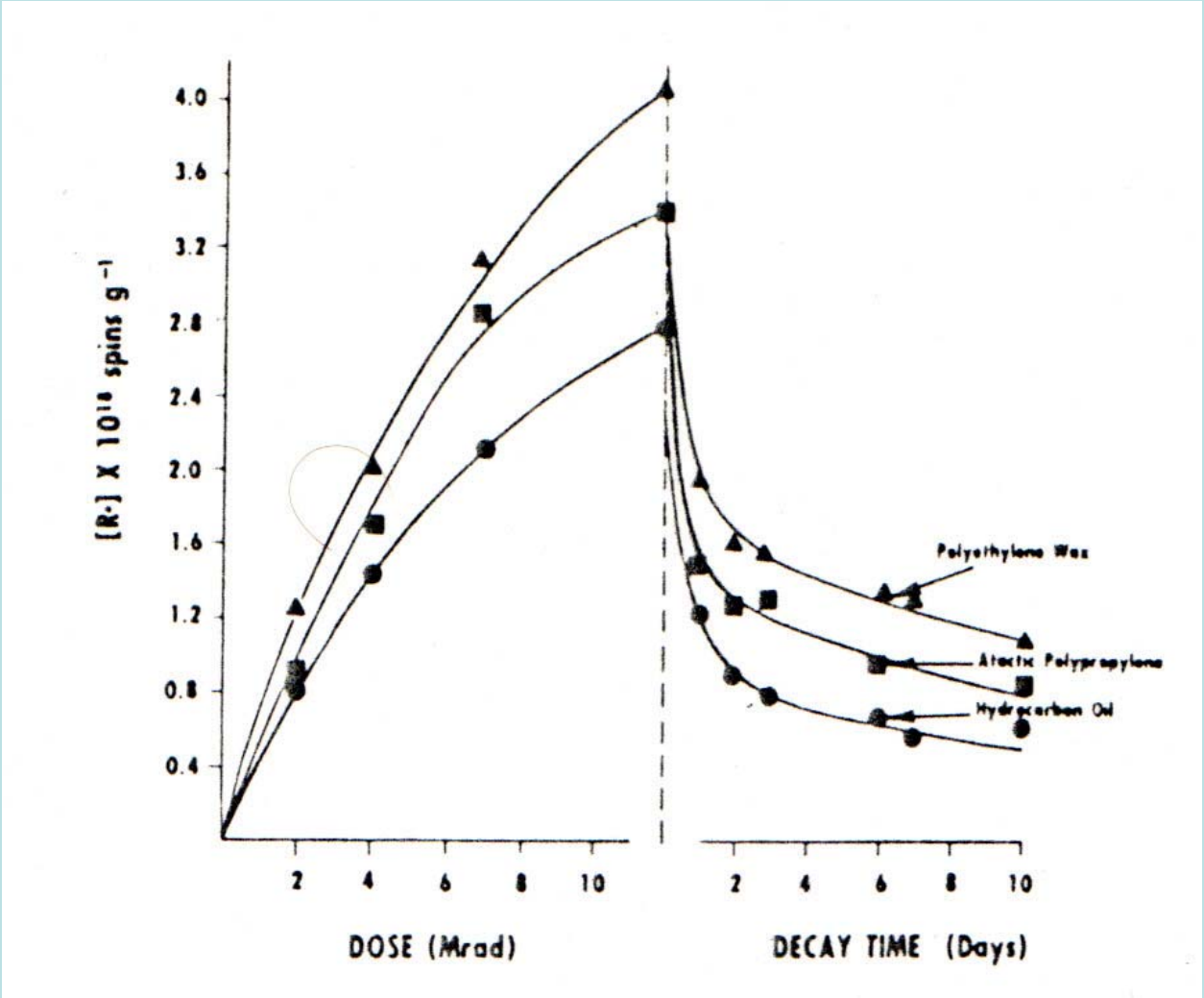


Figure. Radical buildup and decay of γ-irradiated polypropylene containing mobilizing additives of variying molecular weights

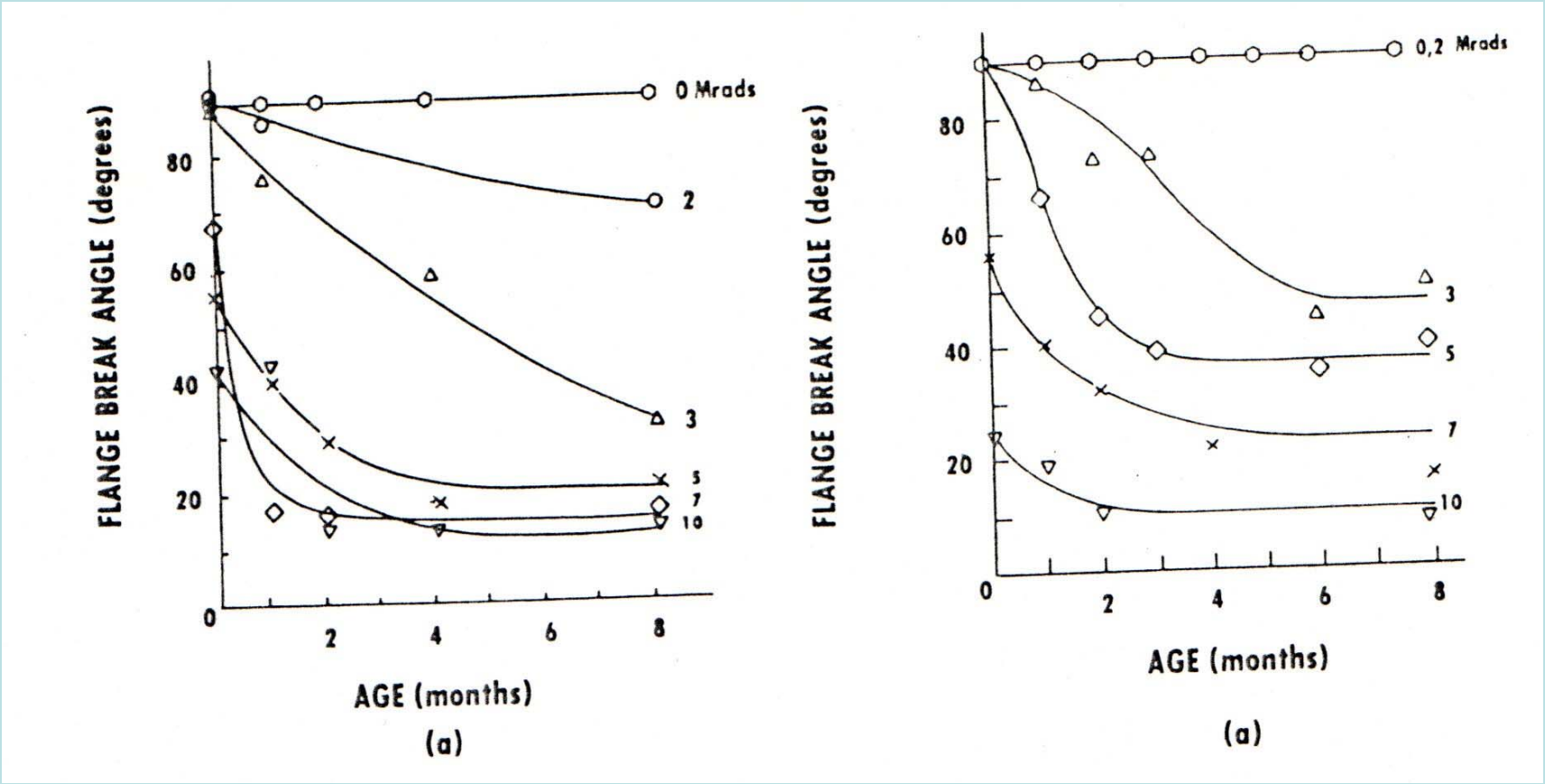


Figure. Mechanical property aging studies on γ-irradiated isotactic polypropylene with 1.2% mobilizing additive (a) flange angle, (b) work

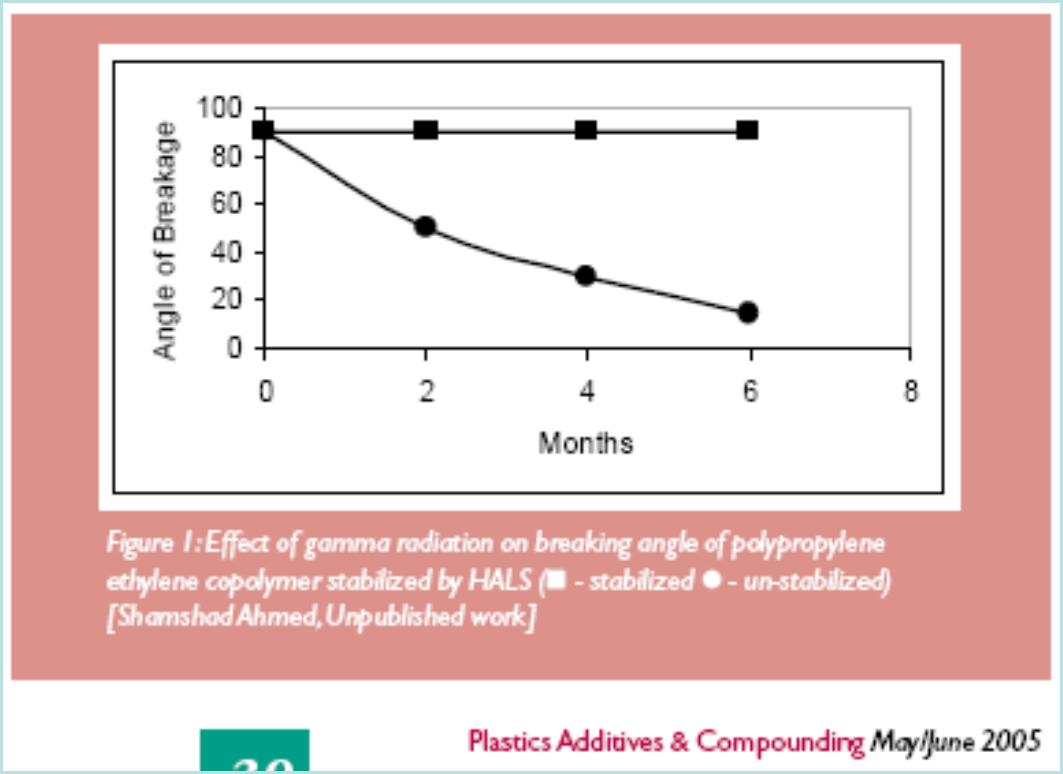


Figure 1: Effect of gamma radiation on breaking angle of polypropylene ethylene copolymer stabilized by HALS (■ - stabilized ● - un-stabilized) [Shamshad Ahmed, Unpublished work]

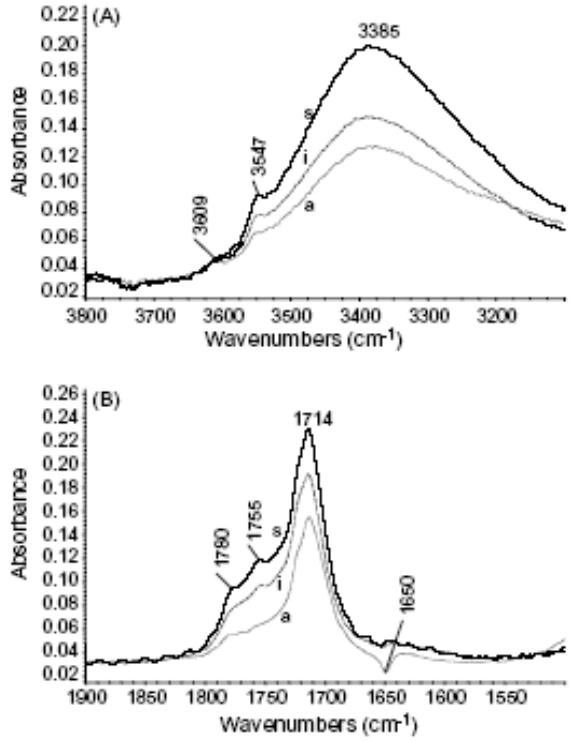


Fig. 4. Subtraction of the initial spectrum from the spectra recorded after irradiation at 48 kGy under oxygen for PPi (i), PPs (s) and PPa (a) films in the 3800–3000 cm^{-1} (A) and in the 1900–1500 cm^{-1} (B) region.

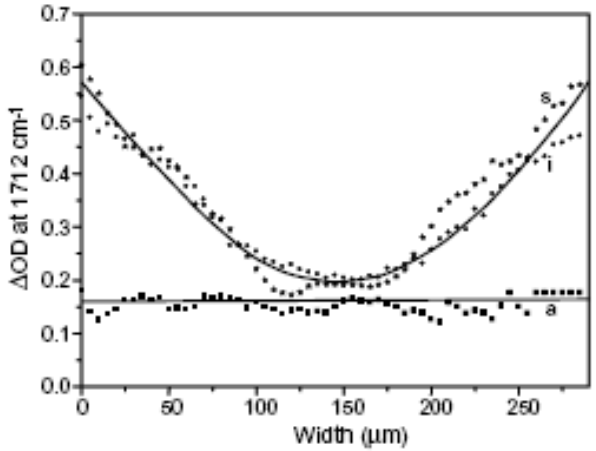


Fig. 7. Oxidation profile measured by micro-FTIR spectroscopy in isotactic (i), smectic (s) and amorphous (a) PP films γ-irradiated under oxygen at 75 kGy and stored at room temperature.

Suppression of Radiation-induced Oxidation in PP

- Additives
- Copolymers
- Coating

Some US Patents

- 4110185: Incorporates immobilizers
- 4113595: Blending with acetylenic compound
- 4431497: Benzhydrol as stabilizer
- 4460445: Hindered phenol stabilizer
- 4931230: Quenching after extrusion
- 6231936: Copolymer with PE
- 7655723: Adding syndiotactic PP into isotactic PP

THANK YOU
FOR YOUR KIND ATTENTION

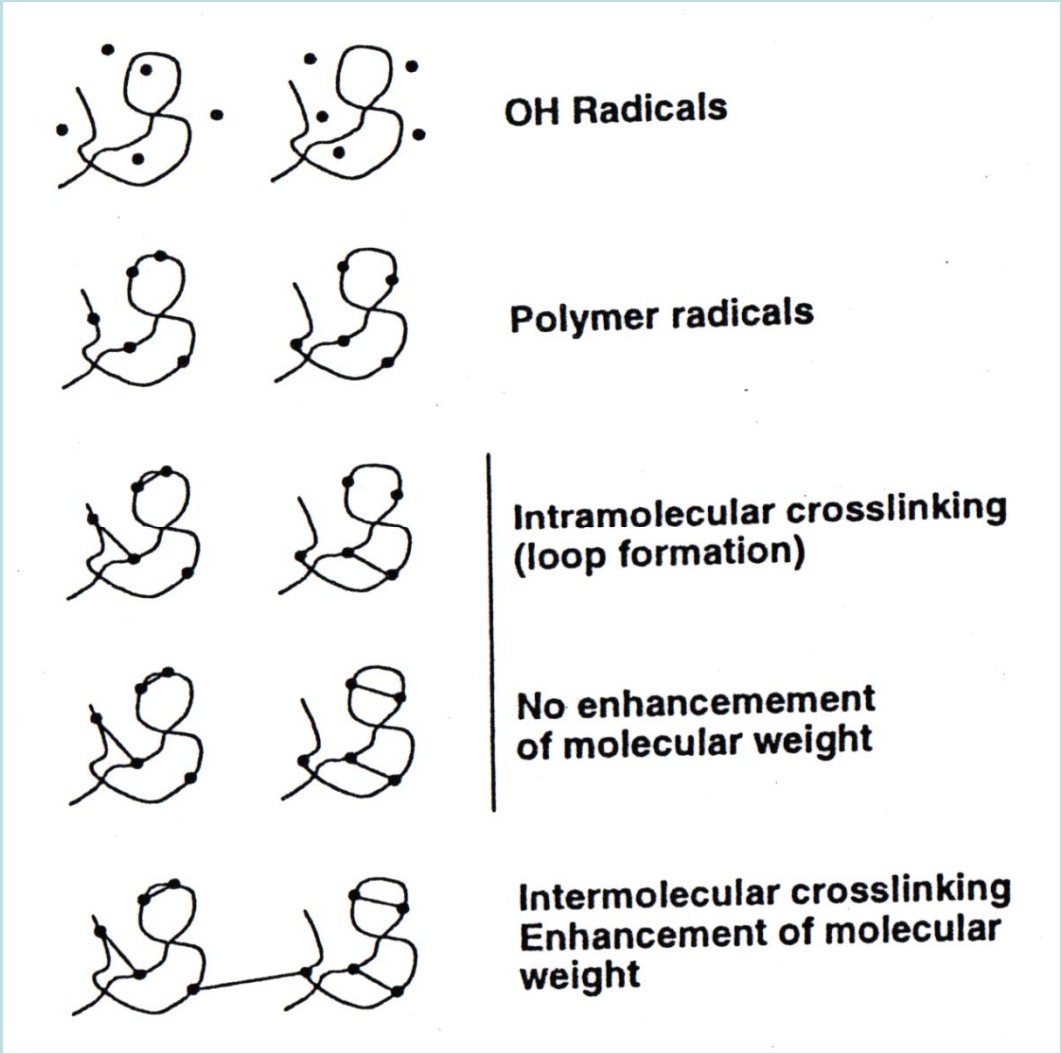
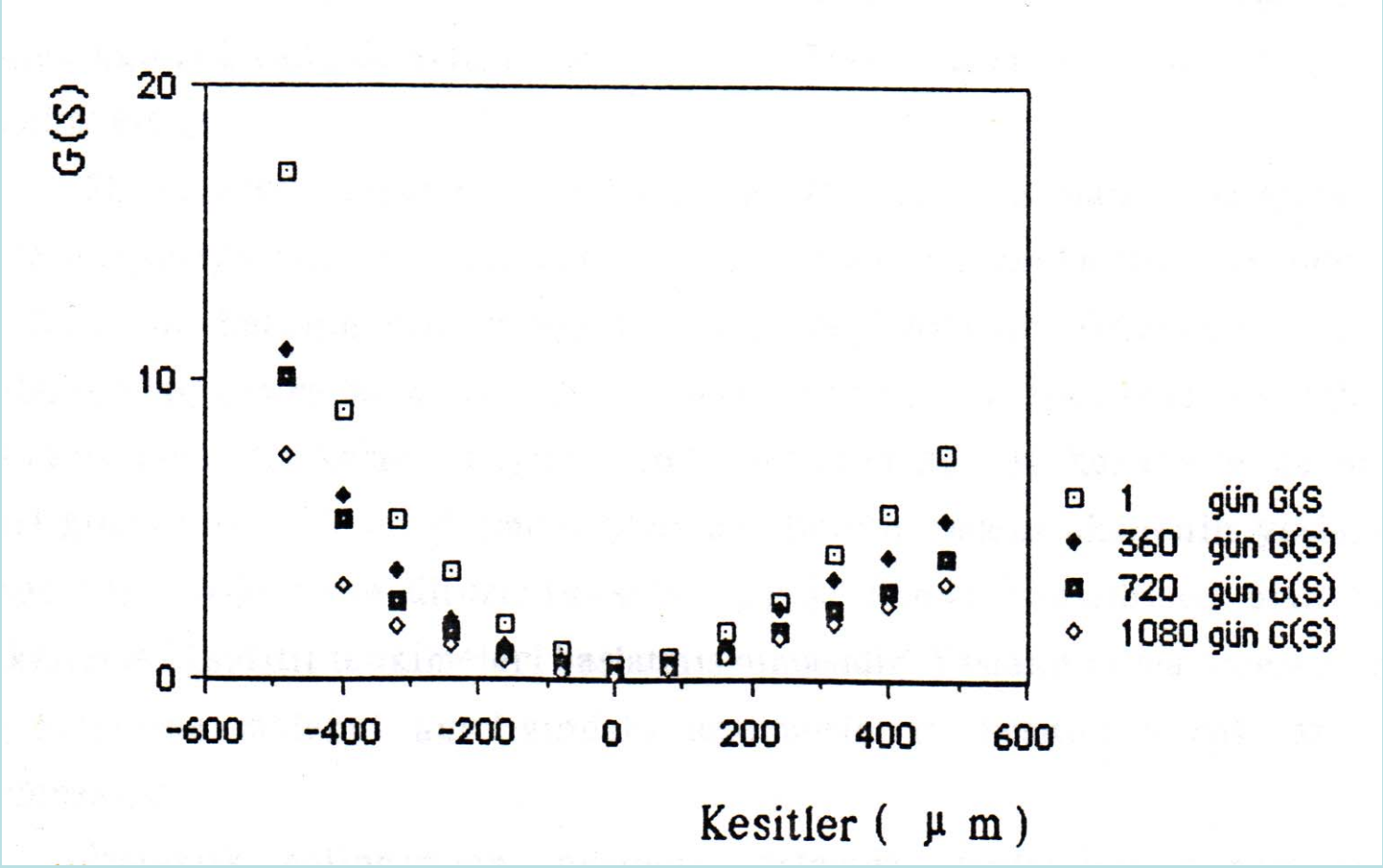


Figure. Schematic description of the formation of intra- and intermolecular crosslinking of polymer radicals



Cross sectional dependence of G(S) value on aging