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Temperature Dependence of Radiation Effects on Polymers

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SUMMARY: Temperature dependence of radiation effect on various polymers including hydrocarbon and fluorocarbon polymers was investigated. Gas evolution and mechanical properties were measured in a wide range of temperatures. G-values of chain scission and crosslinking were estimated. It has been made clear from those experimental results that radiation effect be profoundly affected by temperature. Particularly, significant changes of radiation effect in the melting region were found out.

Introduction

Temperature dependent phenomena are based on vibrational, rotational and transitional motion of molecules. Transitions are important as thermodynamical phenomena due to the segmental motion of polymers such as γ, β, α, glass transitions and melting.

Radiation induced effect on polymers is related greatly to thermodynamical processes such as, diffusion, crystallization, quenching, annealing and various relaxations. Needless to say that radiation effect on polymers depends also very much on the morphological states; whether they are crystal or amorphous, furthermore, the form of crystal, the rigidity of glass and the fluidity of molten state.

The relationship between morphology and molecular structure of polymers is important to

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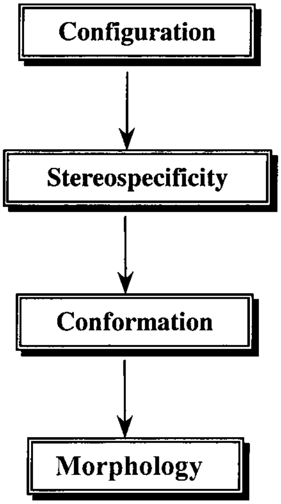
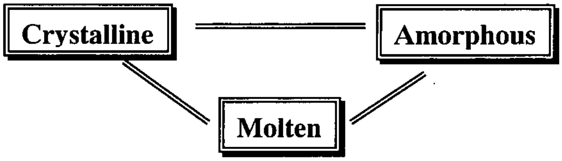
discuss radiation effect on polymers. Regarding the molecular structure, there are configuration and conformation. The configuration is defined as stereo-isomers that are not temperature dependent such as atactic, syndiotactic and isotactic. On the other hand, the conformation is defined as geometrical structure convertible through internal rotation, which is temperature dependent.

The configuration itself is strongly correlated with the radiation effect.



Macroscopically, there are differences in radiation effect among three different states depending on temperature.



Formation of excited states, trapping of active species and reaction of the transient species are involved in the radiation chemical processes.

The processes include in-source and post reactions, such as crosslinking, chain scission, decomposition, polymerization and grafting.

Those radiation-induced chemical reactions from an early stage of excitation or ionization are temperature dependent. Some of interesting recent results are presented in this paper. A general conclusion concerning temperature effect is tried to be derived.

Temperature Dependence of Radiation Effect on Various Polymers

Effect of temperature on radiation effect for various polymers has been examined in a wide range from 4K to the melting temperature of polymers. Main interesting results are summarized.

Experimental

Low density polyethylene, isotactic polypropylene, atactic and syndiotactic polystyrene, polytetrafluoroethylene(PTFE), and fluoro-copolymers were used for the experiments.

Irradiation was carried out under oxygen-free atmosphere in a wide range of temperature region from 77K to the melting temperature of polymers using a special apparatus1).

Various measurements(gas chromatography, gel fraction, mechanical properties, DSC analysis, fluorescence spectroscopy, X-ray diffraction, optical absorption, ESR spectroscopy, solid state ^{19}F NMR spectroscopy and FT-IR spectroscopy) were made.

Results and Discussions

Polyethylene, Model Compounds $CH_3(CH_2)_nCH_3$, n-6~50 2)

Temperature independent formation of H_2 was observed in polyethylene. $G(H_2)$ for ethylene-propylene rubber was measured as a function of pylene concentration. 1.70 was non-scavengeable G-value for the total G-value of 3.30 2). Those are originated from excited cation radical RH^{+*}, followed by crosslinking and C=C bond formation.

For the model compounds, such as linear hydrocarbons from C_{20} to C_{24}, selective crosslinking at the chain end was observed for crystal, while random crosslinking for liquid 3). The difference between crystal and liquid is due to the different conformation in crystal and liquid. Selective end radical formation comes from the zig-zag planer stretched conformation(TT) in crystal. While, random formation of radicals along the chain comes from bended conformation(GT) in liquid[4].

In the early stage of radiation effects on polyethylene and the model compounds, crosslinking and C=C bond formation occur simultaneously. Successive radical formation in the later stage is concentrated to the C=C sites accumulated. Therefore, crosslinking occurs heterogeneously in the whole period of irradiation. The heterogeneity depends upon very much the irradiation dose.

Enhancement of crosslinking takes place through active segmental motion in amorphous[5] and molten state at elevated temperatures.

Polypropylene

According to our old work[6], together with recent experimental results, radiation induced chain scission increases gradually with increasing temperature from about 300K, and the scission increases rapidly from 370K up to the melting point of 430K. G-values of the chain scission increases drastically from G(s)=2.0 to G(s)=5.5 in the molten state as shown in Fig.1[6].

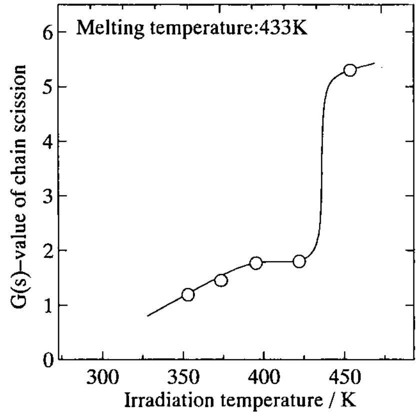


Fig.1 Effect of temperature on chain scission of isotactic polypropylene. Irradiation was made with γ-rays from ^{60}Co source under vacuum.

Post-crosslinking takes place by heating samples irradiated at room temperature to 370K. Elongation at break and tensile strength of isotactic polypropylene(melting temperature:433K) under a constant irradiation dose of 50kGy as a function of irradiation temperature are shown in Figs.2 and 3 together with those of low density polyethylene(melting temperature:383K, ρ:0.92). It is interesting to note that temperature dependence of radiation effect on isotactic polypropylene is quite different from that of polyethylene.

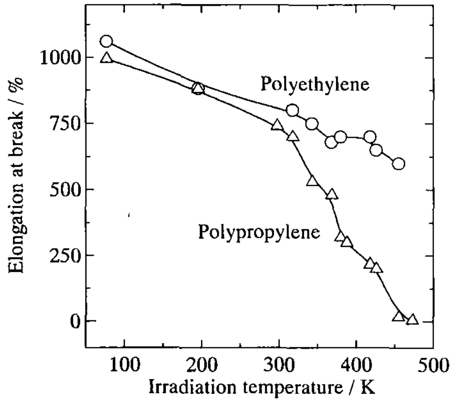


Fig.2 Effect of temperature on mechanical properties of polyethylene and isotactic polypropylene. Elongation at break as a function of irradiation temperature. Irradiation at 77K by γ-rays , and the other temperature by electron beam.

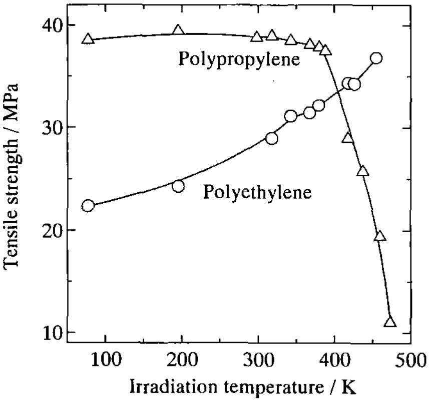


Fig.3 Effect of temperature on mechanical properties of polyethylene and isotactic polypropylene. Tensile strength as a function of irradiation temperature.

Recently, it has been found[7] that syndiotactic polypropylene be better crosslinked compared with isotactic polypropylene. It is interesting to indicate that radiation effect on polymers be strongly affected by their stereoregularity(configuration).

Polystyrene[8,9]

Radiation effects on polystyrene(AA: atactic, $M_W=2.5\times10^5$, SA: syndiotactic, crystalline parts 3 ~ 10%, $M_W=2.6\times10^5$, SC: syndiotactic, crystalline parts 50 ~ 60%, $M_W=2.6\times10^5$) have been examined in a wide range of temperatures from 77K to 430K[8]. Below the glass transition of 370K, clear differences among AA, SA, SC for formation of H_2 have been observed.

$$G(H_2)_{AA} > G(H_2)_{SA} > G(H_2)_{SC}$$

Below 310K, no temperature dependence for the formation of H_2 has been seen. This is indicating that non-scavengeable, fast processes in the low temperature region exist, and the H_2 formation is very much influenced by not only stereoregularity(configuration), but also crystallinity(conformation). Above the glass transition, H_2 production from amorphous parts of syndiotactic polystyrene disappears, because the amorphous parts is converted to crystalline polymer. $G(H_2)$ is shown for three different specimens as a function of temperature in Fig.4.

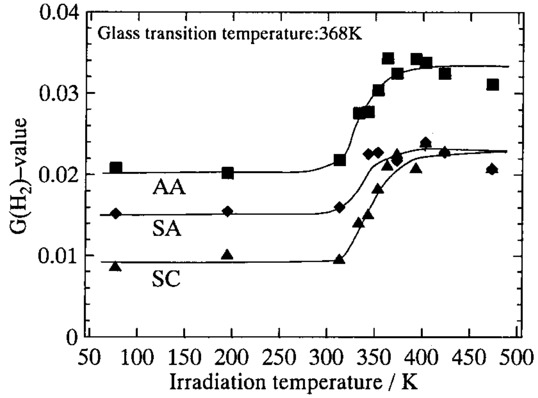


Fig.4 Effect of temperature on formation of hydrogen molecules. G-value of H_2 as a function of irradiation temperature. Irradiation by γ-rays. ■:AA, ◆: SA and ▲: SC.

Temperature dependencies of G(x) and G(s) are shown in Fig.5.

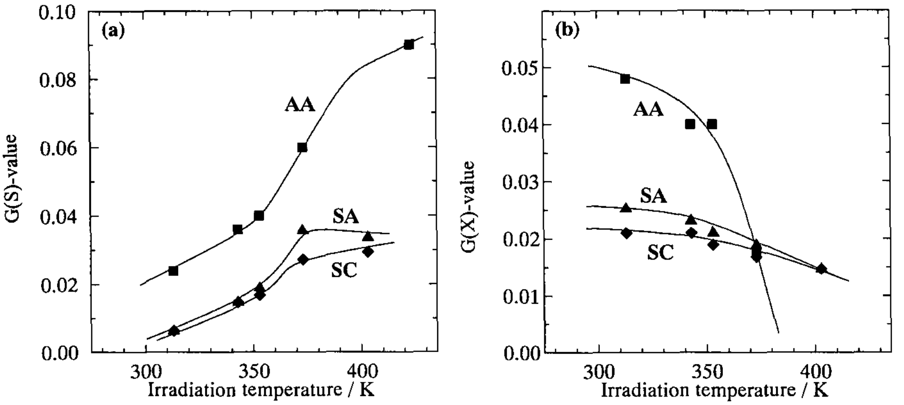


Fig.5 G(x) and G(s) as a function of irradiation temperature for syndiotactic(amorphous and crystal) and atactic polystyrene. (a):G(x)-value, (b):G(s)-value. ■:AA, ▲: SA and ◆: SC

As are obvious from the figure, G(x) decreases with increasing temperature, while G(s) increases with increasing temperature. A small difference between $G(x)_{SA}$ and $G(x)_{SC}$, a significant difference between $G(x)_{AA}$ and $G(x)_{SA,SC}$ were observed. A similar tendency was observed for G(s).

$$G(x)_{AA} > G(x)_{SA} > G(x)_{SC}$$

$$G(s)_{AA} > G(s)_{SA} > G(s)_{SC}$$

Emission spectra from excimer in those specimens are shown in Fig.6.

As is seen from the figure, there exists significant difference in the spectrum among E_{AA}, E_{SA} and E_{SC}.

It has been shown in our previous papers that the lower the excimer level, the higher the stability against radiation. This tendency does not contradict with the orders of $G(H_2)$, G(x) and G(s).

$$E_{AA} \geq E_{SA} > E_{SC}$$

E is energy level for excimer. From those experimental results mentioned above, it has been clearly demonstrated that radiation effect is affected by not only crystallinity(conformation), but also stereoregularity(configuration) of polystyrene.

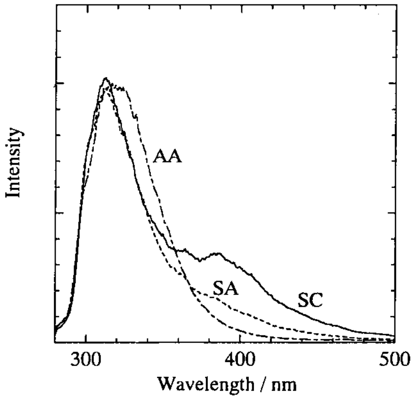


Fig.6 Emission spectra excited with 260nm at room temperature from excimer of three different polystyrene. AA: atactic, SA: syndiotactic-amorphous, SC: syndiotactic-crystalline.

From the ratio of G(x) to G(s), it became clear that polystyrene be predominantly crosslinked at room temperature, while the polymer be degraded effectively at rather higher temperatures above glass transition around 370K.

On the other hand, mechanical properties are improved very much by irradiation at room temperature, while severe deterioration occurs at relatively high temperatures above 400K.

Polytetrafluoroethylene PTFE[8,10-21)]

In our previous papers[10,11)], it was reported that PTFE can be crosslinked by irradiation in molten state. Some of recent results related to radiation effect including crosslinking are now introduced.

Molecular weights as a function of irradiation dose for four different irradiation temperatures

77K, 273K, 573K and 613K are shown in Fig.9.

Except 610K, molecular weights decrease very rapidly with increasing irradiation dose for all other temperatures. For irradiation at 610K in the molten state, molecular weight drops in a small dose, and then increase greatly with increasing irradiation dose. It indicates that chain scission proceeds effectively at 77K, 273K and 573K, while crosslinking occurs at 613K in the molten state. The fastest decrease in the molecular weight is at 573K below the melting temperature of 600K.

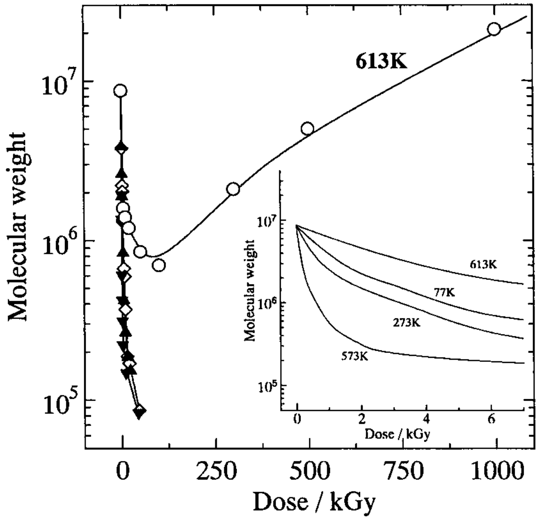


Fig.7 Molecular weight against dose for irradiated PTFE with γ-rays under vacuum at 77K(◇), 273K(▲), 573K(▼) and 613K(○).

G-value of chain scission in a wide range of temperatures from 77K to 613K is shown in Fig.8 as a function of irradiation temperature[12].

It is interesting to note that G-values increase discontinuously at γ(176K), β(292K-303K) and α(403K) relaxation, stepwise. It suggests that chain scission is enhanced by molecular motion along the chain axis and by inter-crystallites long-range molecular motion.

Heat of crystallization(ΔH_C) as a function of irradiation dose for 77K, 300K, and 613K is shown in Fig.9[8,11,12].

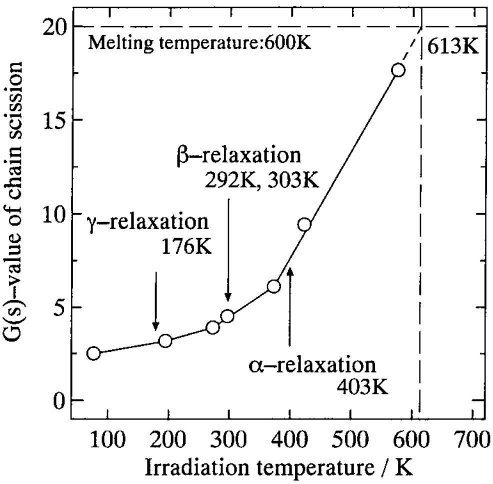


Fig.8 Relationship between G-value of scission G(s) and irradiation temperature for PTFE irradiated with γ-rays under vacuum.

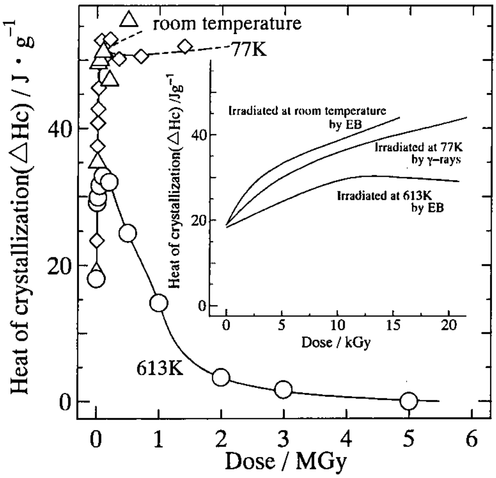


Fig.9 Heat of crystallization(ΔH_C) against dose for irradiated PTFE under oxygen-free atmosphere at 77K(◇), room temperature(△) and 613K(○).

It is demonstrating that crystallization proceeds rapidly due to effective chain scission for irradiation at 77K and 300K, while crystallization proceeds to some extent at an early stage of irradiation at 613K, and then crystalline parts of PTFE decreases rapidly irradiation dose and finally crystalline parts disappear completely for irradiation in the molten state. The decrease in ΔH_C corresponds to the increase in crosslinking.

Elongation at break and tensile strength are plotted in Fig.10 as a function of irradiation temperature for PTFE irradiated with a dose of 100kGy under oxygen-free atmosphere[8].

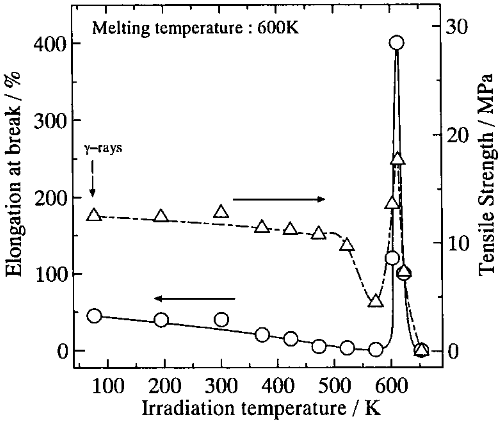


Fig.10 Relationship between mechanical properties and irradiation temperature for PTFE irradiated with 100kGy under oxygen-free atmosphere. ○:Elongation at break and △: Tensile strength.

Sharp increase in both values at melting temperature is due to crosslinking formation in this temperature region.

Plots of Young's modulus against irradiation dose for irradiation at 77K, 300K and 613K are shown in Fig.11.

Young's modulus increases significantly with increasing irradiation dose only for PTFE irradiated at melting temperature. This is also clearly indicating that crosslinking takes place only at 613K±10K.

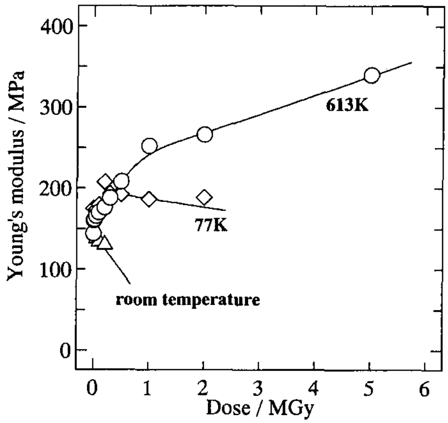
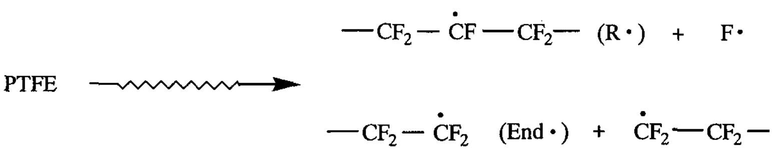


Fig.11 Young's modulus against dose for irradiated PTFE under oxygen-free atmosphere at 77K(◇), room temperature(△) and 613K(○).

Estimation of G-Value of Crosslinking[12,16)

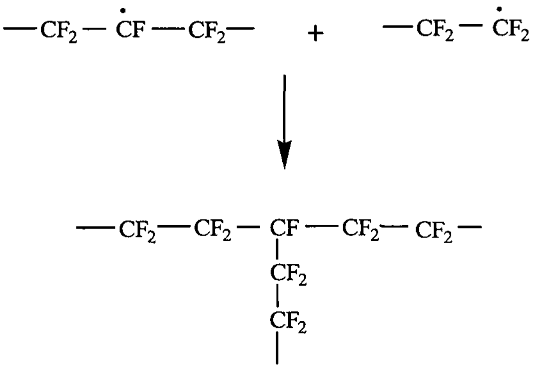
According to electron spin resonance measurements of irradiated PTFE, formation of alkyl radical(R•) and scission type(End•) radical has been observed. The formation ratio of both alkyl radical and scission type radical is 10 : 1, respectively[17).



$$\text{PTFE} \rightsquigarrow \begin{cases} -CF_2-\dot{C}F-CF_2- \ (R\bullet) + F\bullet \\ -CF_2-\dot{C}F_2 \ (End\bullet) + \dot{C}F_2-CF_2- \end{cases}$$

G-value of trapped free-radicals(G(radicals)) at 77K and 297K were obtained recently to be 0.38 and 0.14 in our experiments[12,18).

On the other hand, G(End•) can be estimated from G(s) measured by molecular weight as shown in Fig 8. G(End•) = 2 × G(s) $\cong$ 40 at melting temperature. G(radicals) at 77K, 0.38 could correspond to a value in an early stage of radiation induced reaction, and it would be assumed to be the lowest value of G(radicals) during irradiation in the molten state. Therefore, in the molten state of PTFE during irradiation, crosslinking could be formed by encountering of excess number of end radicals $-CF_2\cdot$ (G = 40) with a small number of alkyl radical (G≥0.35=0.38×10/11). As the concentration ratio be less than 1/100, T-type crosslinking would be predominant. Therefore, G(x) is evaluated to be more than 0.35.



After crosslinking in the molten state, the crosslinked PTFE specimens with various degree of crosslinking were irradiated again at 77K and 297K. G-value of trapped free radicals formed was plotted as a function of degree of crosslinking(expressing by irradiation dose for crosslinking), as shown in Fig.12[18)].

For specimens irradiated at 77K, G(radicals) measured at 77K increases from 0.38 to 3.6 as the crosslinking density increases. On the other hand, G(radicals) measured at 297K increases from 0.14 to 3.2 for specimens irradiated at 297K. It is surprising that G(radicals)-values for higher densities of crosslinking are 10 to 20 times higher in the concentration of radicals than that for non-crosslinked PTFE. This can be explained by production of tertiary alkyl radicals through either selective energy or charge transfer to the crosslinking site, or dissociative electron attachment at the crosslinking site.

G-value for crosslinking estimated from the density of tertiary alkyl radicals does not contradict with G-value obtained from alkyl radical observed at 77K.

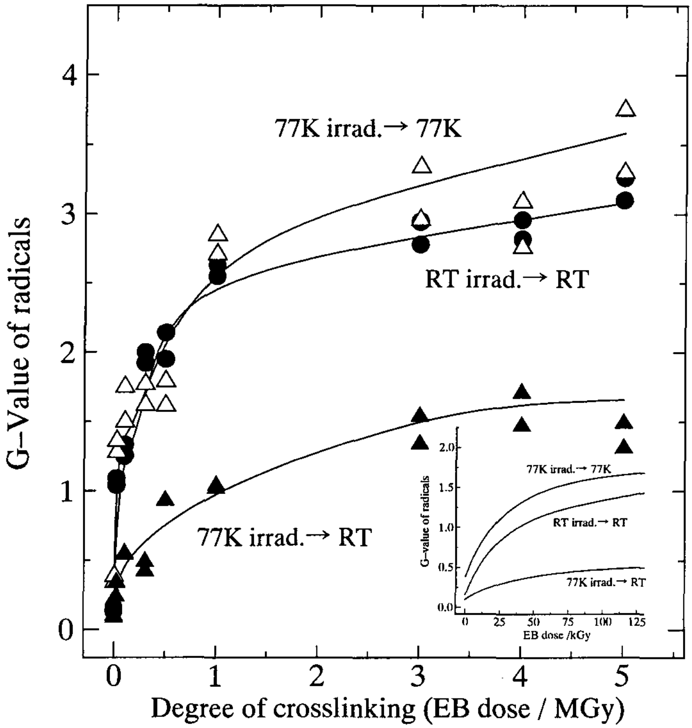


Fig.12 G-value of free radicals trapped in crosslinked PTFE by γ-irradiation at 77K and room temperature. △: 77K irradiation, ▲: room temperature after 77K irradiation and ●: room temperature irradiation.

High resolution solid state ^{19}F high-speed(HS) magic angle spinning(MAS) NMR spectra of crosslinked PTFE is shown in Fig.13[16]. Signal assignments have been made and the results are summarized in attached table.

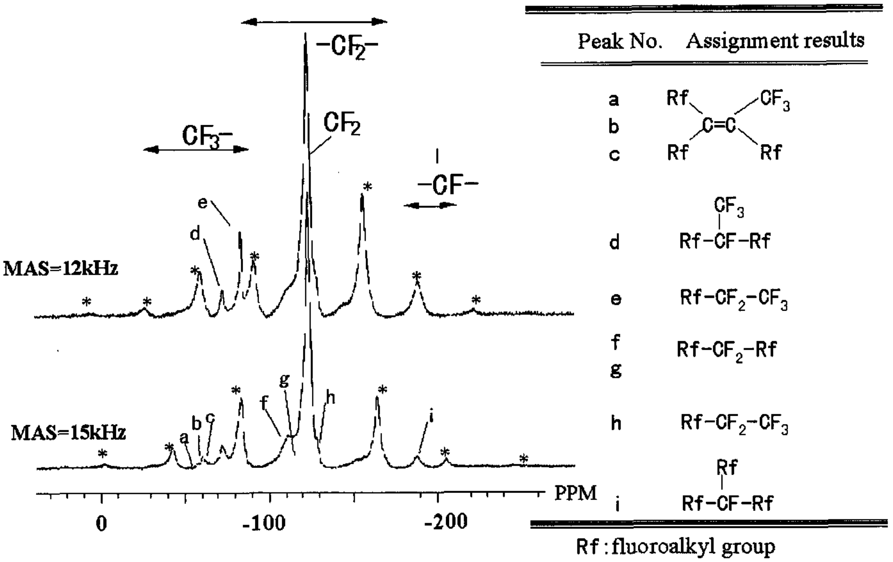
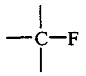


Fig.13 High-resolution solid-state ^{19}F HS MAS NMR spectra of crosslinked PTFE(10MGy-crosslinking) with signal assignments.

Crosslinking sites were able to detect, and the concentration of  $-\overset{|}{\underset{|}{C}}-F$ could be estimated.

From those experimental results, G(x) was summarized as a function of irradiation dose for crosslinking in Table 1.

Table 1 Crosslinking density and G(x)-value of crosslinking for PTFE[16)].

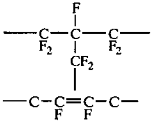
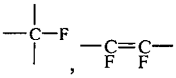
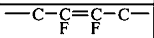
Dose / MGy	Crosslinking density* / %	G(x)
0	0	-
0.5	Trace	-
1	0.21	0.42
2	1.84	1.85
5	2.72	1.08
10	4.06	0.82

*: Estimated from signal intensity of CF versus total signal intensity using ^{19}F HS MAS NMR spectra at spinning rate 15 kHz.

$6I(CF)/[6I(CF)+3I(CF_2)+2I(CF_3)]$

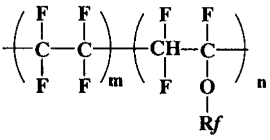
Radiation effects on PTFE at various temperatures are summarized for all items made in our laboratory in Table 2.

Table 2 Radiation effect on PTFE at various temperatures.

Irradiation temp. Item. observ.	4K & 77K	297K	613K	Remarks
Radiation effect	Chain scission	Chain scission	Crosslinking	γ & EB irradiation
Molecular weight 8.7×10^6	8kGy	2kGy		Dose for reduction to 1/10 of initial value.
Elongation at break Initial 400%	9.6kGy	2.5kGy		Dose for reduction to 1/2 of initial value.
Elongation at break Initial 400%	50%	0%	400%	For irradiation dose of 100kGy
Tensile strength initial 55MPa	13MPa	4MPa	18MPa	For irradiation dose of 100kGy
Young' modulus initial 140MPa	No change	Decrease	Increase	With increasing dose
DSC	50J/g	44J/g	30J/g	For irradiation dose of 100kGy
X-ray diffraction	Crystal	Crystal	Amorphous	After irradiation
Solid state ^{19}F NMR[16)				F-resonance  $-\overset{\vert}{\underset{\vert}{C}}-F$, $-\underset{F}{C}=\underset{F}{C}-$ Confirm
FT-IR			 $-C-\underset{F}{C}=\underset{F}{C}-C-$	C-F stretching -C=C- confirm
ESR: concentration, Trapped radical[18)	Low Alkyl, Scission	Low Alkyl, Scission	Very high Tert-Alkyl	After irradiation at each temperature. Irradiated again at RT.
Stability against Radiation[19)	Medium	Very low	High	After irradiation at each temp, re-irradiation was made at RT. Then mechanical properties were measured.
Logarithmic Decrement[20,21)	α-relaxation β-transition γ-relaxation	α-relaxation β-transition γ-relaxation	α-relaxation (-) shift β-Disappear at 600K γ-relaxation (+) shift	Inter-crystallites to inter-crosslinks Helical transition at crystalline Local mode $-CF_2-$
Optical transparency	Non	Non	Yes, 90% at 340nm	0.5mm film

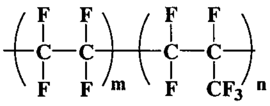
Fluoro-Polymers[14)]

Temperature dependence of radiation effects on fluoro-copolymers — (1) copolymer of C_2F_4 and perfluoroalkylvinylether: PFA, (2) copolymer of C_2F_4 and hexafluoropropylene: FEP and (3) copolymer of C_2H_4 and C_2F_4: ETFE — was examined by thermal and mechanical properties. The molecular structure of fluoro-copolymers using for the experiments are represented as follows,



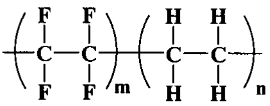
$$\left(-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\right)_m\left(-\underset{F}{\overset{F}{CH}}-\underset{\underset{Rf}{O}}{\overset{F}{C}}-\right)_n$$

(1) PFA(MT:583K)



$$\left(-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\right)_m\left(-\underset{F}{\overset{F}{C}}-\underset{CF_3}{\overset{F}{C}}-\right)_n$$

(2) FEP(MT:543K)



$$\left(-\underset{F}{\overset{F}{C}}-\underset{F}{\overset{F}{C}}-\right)_m\left(-\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}-\right)_n$$

(3) ETFE(MT:538K)

Melting temperature, crystallization temperature, heat of crystallization, elongation at break and tensile strength were measured as a function of irradiation temperature. It has been made clear that all fluoro-copolymers have similar tendency on irradiation effect. That is, crosslinking proceeds extensively in their molten state without exception and crystallinity decreases to large extent. Phenomena similar to those of PTFE occur in the wide range of temperatures from 77K to their melting temperatures. Some of experimental results are shown in Figs.14 and 15. Figure 14 shows thermal properties of fluoro-copolymers under a constant irradiation dose(PFA:100kGy, FEP:500kGy and ETFE:1MGy) as a function of irradiation temperature, and also Fig.15 shows mechanical properties as a function of irradiation temperature.

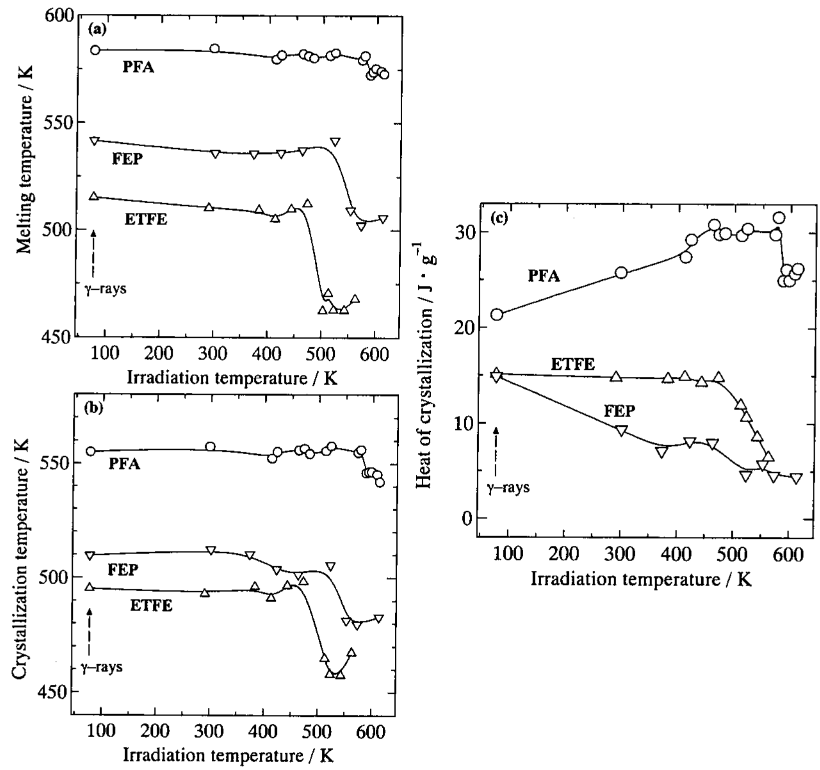


Fig.14 Thermal properties as a function of irradiation temperature for three fluoro-copolymers(PFA, FEP and ETFE). (a) Melting temperature, (b) crystallization temperature and (c) heat of crystallization.

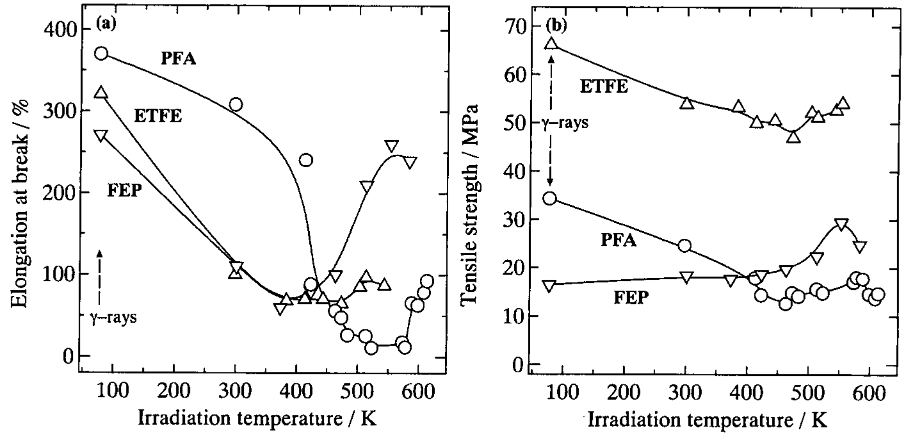


Fig.15 Mechanical properties as a function of irradiation temperature for three fluoro-copolymers(PFA, FEP and ETFE). (a) Elongation at break and (b) Tensile strength.

Summary of Recent Experimental Results

Gas evolution and G-values of crosslinking and chain scission, and mechanical properties for various polymers are summarized in connection with temperature dependencies on radiation effect, as shown in Table 3-5.

Table 3 Temperature dependence of radiation-induced gas evolution in various polymers.

Irradiation Temp.		77	RT	Tg	MT
Polyethylene		$H_2(h)$ ≈	$H_2(h)$ <	$H_2(h+t)$ <	$H_2(h+t)$
Model Compounds[2]					
(C_{20}-C_{24})		CH_4	CH_4 ≤	CH_4 <	CH_4
C_2H_6: Odd number only			C_2H_6 ≤	C_2H_6 <	C_2H_6
Polystyrene[8]	AA	$H_2(h)$ ≈	$H_2(h)$ <	$H_2(h+t)$	
$G(H_2)$:	SA	$H_2(h)$ ≈	$H_2(h)$ <	$H_2(h+t)$	
AA>SA>SC	SC	$H_2(h)$ ≈	$H_2(h)$ <	$H_2(h+t)$	
$G(CH_4)$		CH_4 (very Low)		CH_4 (Significant)	
				AA<<SA	
				AA<<SC	
PMMA[22]		$H_2(h)$ ≈ CO, CO_2 <<	$H_2(h)$ < CO, CO_2 <	$H_2(h+t)$ CO,CO_2	
GFRP[22]		$H_2(h)$ ≈	$H_2(h)$ <	$H_2(h+t)$	
Glass Fiber Reinforced Plastic		CO, CO_2 <<	CO, CO_2 <	CO, CO_2	

h: hot, non-scavengeable
t: thermal, scavengeable
AA: Atactic Polystyrene
SA: Amorphous Syndiotactic Polystyrene
SC: Crystalline Syndiotactic Polystyrene
GFRP: Bisphenol-A and Aliphatic amine

Tables. 4 & 5(Next page)

Temperature dependencies of radiation effect on polymers could be explained through conformational change directly, and configurational characteristics indirectly.

In general, radiation-induced physico-chemical processes in polymeric systems are usually very selective, and have heterogeneous natures. Interesting several new examples in conjunction with those respects have been shown in this paper.

Table 4 Temperature dependence of G(x) and G(s) in various polymers.

Polymers	Rigid	Molten	Remarks
Polyethylene	G(x)	G(x)↑	
Model compounds	End-linking	Center-linking	C_{20}~C_{50}
Polypropylene			
I: isotactic	G(x), G(s)	G(s) ↑	Drastic change of G(s)
S: syndiotactic[7)]	G(x), G(s)	G(s) ↑	$G(x)_S > G(x)_I$
Polystyrene			
AA: atactic	$G(x)_{AA}$, $G(s)_{AA}$	$R = G(s)/G(x)$	Significant increase above Tg
SA: syndio-amorphous	∨ ∨		
SC: syndio-crystalline	$G(x)_{SA,SC}$, $G(s)_{SA,SC}$	$R_{AA} >> R_{SA,SC}$	
	G(x),G(s): SA≒SC		
Polytetrafluoroethylene	G(s)↑	G(x)↑	G(x): Sharp increase at MT G(s): Rapid increase with temperature below MT
Fluoro-copolymers			
PFA	G(x) < G(s)	G(x)↑,G(s)	Acceleration of crosslinking around MT
FEP	G(x) < G(s)	G(x)↑,G(s)	
ETFE	G(x) ≥ G(s)	G(x)↑,G(s)	
Polysulfone(PSF)[23)]	G(x), G(s)	G(x)↑	Significant increase above Tg

Table 5 Temperature effect on radiation-induced mechanical properties of various polymers.

Irradiation Temp.(K) Polymers		4	77	RT	Tg	MT
Polyethylene	50kGy		1.0	1.3↑		1.6↑
Polypropylene	50kGy		1.0	1.0↓		0.25↓
Polystyrene	Wide range			+	– ↓	
Polytetrafluoroethylene	10kGy	1.0[24)]	1.0	0.2		0.65↑
PMMA*[15)]	100kGy		1.0	0.14↓		
GFRP*[15)]	1MGy		1.0	0.07↓		

*:Flexural strength, other polymers by tensile strength. Relative values.

Conclusion

Effect of radiation on polymers depends upon very much their morphology. The morphology depends on directly conformation and segmental motion of polymer chain which are temperature dependent. Significant differences in radiation effect have been found not only in different morphologies(conformation), but also in different stereoisomers(configuration).

Therefore, radiation effect is very much temperature dependent. This can be explained by mode of segmental motion of polymer chain. Not only slow thermal process, but also fast-, non-scavengeable process in radiation-induced phenomena are dependent on both "conformation" and "configuration" of polymers. Not much systematic studies from this viewpoint have been carried out up to now. This research field will open the frontiers in radiation chemistry in polymers.

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