

Chapter 2

Chemistry of High-Energy Charged Particles: Radiations and Polymers

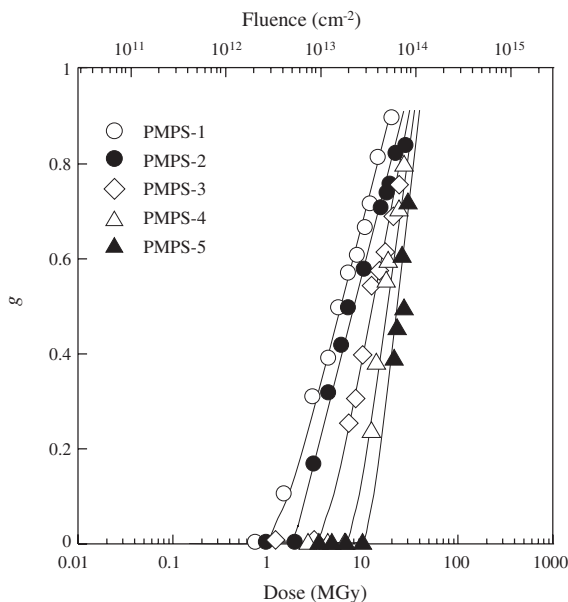
The combination of polymers and the high-energy charged particles with sufficiently high LET is the promising candidate for the feasibility of the concept: “A particle producing a material.” The radiation sensitivity of polymers has been widely and extensively discussed in the field of radiation chemistry, and here we focus onto the phenomena upon irradiation to high-energy charged particles. The radiation-induced reactions in polymers generally depend on the nature of radiation sources, especially the value of LET [1–3], because of the secondary reactions among reactive intermediates produced by radiations. Among a variety of polymeric materials, Si backbone polymers; polysilanes are the simple but interesting motifs exhibiting drastic shift of the major reactions from main chain scission to cross-linking with an increase in the value of LET [4, 5]. Here, the first example of the incarnation of the concept is discussed with this polymer motif.

The cross-linking reactions in the polymeric systems are often promoted by the coupling reactions between neutral reactive intermediates, and the polysilane systems demonstrated effective formation of silyl radicals with relatively high stability to the carbon centered radical analogs [6, 7]. The coupling reactions seemed to occur within an ion track, leading to give an insoluble “nanogel” along each corresponding particle, and produce wire-like 1D-nanostructures via isolation of “nanogel” on a substrate by removing soluble uncross-linked parts [8–16].

The first demonstration is the simple three step protocol: coating of the polymers onto Si substrates at 0.2–1.0 μm thick, irradiation to a variety of MeV order high-energy charged particle from several accelerators in vacuum chambers, and washing the film in solvents to remove uncross-linked parts of the film [7, 15, 16]. After the washing and drying procedures, surface morphology of the substrate with the “nanogels” was observed directly by an atomic force microscope (AFM).

Striking contrast to the highly sensitive main chain scission reaction of polysilanes upon exposure to UV light, X-rays, and high-energy charged particle irradiation of films was found to cause gelation of the polymers for all particles, all

Fig. 2.1 Sensitivity curves (gel evolution curves) for PMPS with various molecular weights ($M_w = 68\text{--}33$ (PMPS-1), 20–16 (PMPS-2), 3.6–3.0 (PMPS-3), 1.5–1.2 (PMPS-4), 0.71–0.60 (PMPS-5) $\times 10^4 \text{ g mol}^{-1}$) under irradiation with a 2 MeV $^4\text{He}^+$ particles. Reprinted with permission from Seki et al. 2005. ©2005, American Chemical Society (Ref. [14])



energies, and all molecular weights of poly(methylphenylsilane) (PMPS). Since the first synthesis of soluble polysilane derivatives, the effective backbone fragmentation via excitation of the σ -bonds in their main chains had been motivated to use the derivatives as a candidate for sensitive resist materials in the lithography processes. The results of high-energy charged particle irradiation are reversed completely, and this is the case of the radical coupling reaction in the extraordinary high density of the intermediate in an ion track. Macroscopic gelation behavior of PMPS is represented by the sensitivity (gelation) curves as shown in Fig. 2.1; total gel volume evolution with the irradiation of 2 MeV He^+ particles with the value of LET as 220 eV nm^{-1} .

In Fig. 2.1, the gel fraction increased dramatically with the absorbed dose (D), reaching up to 1 where the entire polymer film becomes insoluble against any kind of solvents. Yields of radiation-induced reactions have been expressed as G -values, where G is the number of molecules changed (produced or damaged) per 100 eV energy absorbed by the media. This quantification of the chemical yields were already introduced by the initial analysis of the reactions in the polymer materials by Charlesby [17] and the characteristic yields of cross-linking and main chain scission are given by $G(x)$ and $G(s)$, respectively. According to the statistical theory of the reactions, the values of $G(x)$ and $G(s)$ can be estimated by the following Charlesby–Pinner relationship [18]

$$s + s^{1/2} = \frac{1}{q}(p + m M_{n,0} D) \quad (2.1)$$

$$s = 1 - g \quad (2.2)$$

Table 2.1 $G(x)$ measured for PMPS with a variety of molecular weight upon irradiation to high-energy charged particles^a

Polymers	Molecular weight (/10 ⁴ kg mol ⁻¹)	$G(x)$				
		2 MeV H 15 eV/nm	2 MeV He 220 eV/nm	0.5 MeV C 410 eV/nm	2 MeV C 720 eV/nm	2 MeV N 790 eV/nm
PMPS-1	68–33	0.0018 (0.0021) ^b	0.0049 (0.0052) ^b	0.021 (0.022) ^b	0.072 (0.0079) ^b	0.082 (0.0095) ^b
PMPS-2	20–16	0.0021	0.0095	0.052	0.081	0.15
PMPS-3	3.6–3.0	0.0030	0.019	0.07	0.18	0.21
PMPS-4	1.5–1.2	0.0075	0.021	0.075	0.20	0.26
PMPS-5	0.71–0.60	0.019 (0.021) ^b	0.061 (0.089) ^b	0.18 (0.19) ^b	0.27 (0.33) ^b	0.34 (0.42) ^b

^aAll the data are quoted from Refs. [3, 8, 14]^bValues in the parenthesis were estimated by Eqs. (2.5) and (2.6)

$$G(x) = 4.8 \times 10^3 q \quad (2.3)$$

$$G(s) = 9.6 \times 10^3 p \quad (2.4)$$

where p and q are the probability of scission and cross-linking, s and g are sol and gel fractions traced, m is the molecular weight of a monomer unit, and $M_{n,0}$ is the number average molecular weight before irradiation. The $G(x)$ values are calculated using these equations for irradiation of PMPS-1 with 2 MeV He⁺, H⁺, C⁺, and N⁺ particles are compared in Table 2.1.

It is obvious that the values of $G(x)$ depends on the molecular weight of the polymers, especially for high LET charged particles. Besides chain length, there are no differences in the chemical structures of the polymers, thus $G(x)$ values should be identical for all polymers to a first approximation.

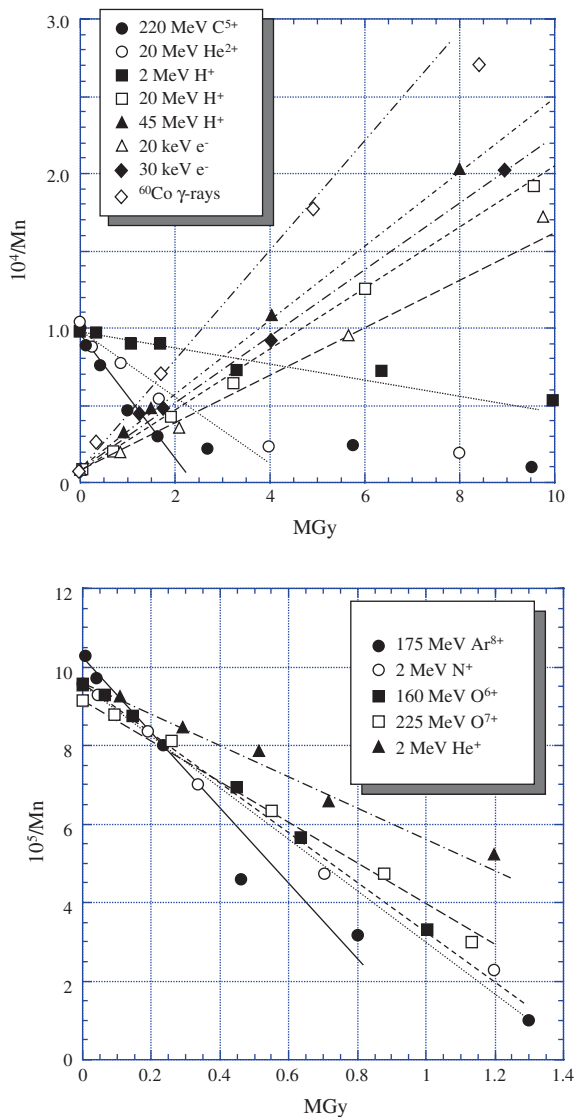
The Charlesby–Pinner equation of (2.1) is reduced to a function of M_n and M_w (number and weight average molecular weight) as follows:

$$\frac{1}{M_n} = \frac{1}{M_{n,0}} + \left(p - \frac{q}{2}\right) \frac{D}{m} \quad (2.5)$$

$$\frac{1}{M_w} = \frac{1}{M_{w,0}} + \left(\frac{p}{2} - q\right) \frac{D}{m} \quad (2.6)$$

where $M_{w,0}$ is the initial weight average molecular weight of the target polymer before irradiation. Poly(di- n -hexylsilane) (PDHS) is the polymer with the identical Si backbone to PMPS, and stable neutral radical formation has been observed upon irradiation to UV and γ -rays through Si–Si σ -bond homolytic cleavage [5]. The relatively long linear alkyl chains (n -hexyl) in contrast to PMPS are expected to act as the source of alkyl radicals, which is the primary choice to promote effective cross-linking reactions in conventional carbon-based polymer materials. The concerted effects of the stable silyl radicals and reactive alkyl radicals were

Fig. 2.2 Charlesby–Pinner plotting of M_n to absorbed dose for 2 MeV $^4\text{He}^+$, 225 MeV $^{16}\text{O}^{7+}$, 160 MeV $^{16}\text{O}^{7+}$, 2 MeV $^{14}\text{N}^+$, 175 MeV $^{40}\text{Ar}^{8+}$, 220 MeV $^{12}\text{C}^{5+}$, 20 MeV $^4\text{He}^{2+}$, 2–45 MeV $^1\text{H}^+$, 20–30 keV e^- , and ^{60}Co γ -rays. Reprinted with permission from Seki et al. 1999. ©1999, American Chemical Society (Ref. [4])



of interest to reveal the mechanisms, efficiency, and yields of cross-linking reactions depending on the density of the reactive intermediates. Here, Fig. 2.2 shows the change of M_n with an increase in the absorbed dose of a variety of radiations, suggesting the clear changes in the slope of the linear relationship. As given in Eqs. (2.5) and (2.6), the slope determines the balance of reaction sufficiency of main chain scission and cross-linking, and the inversion of the slope from positive to negative ones indicate clearly the dominant reaction caused by the radiation from main chain scission (breakdown of the polymer chain) to cross-linking

(gelation). It should be noted that the change in the slope shift gradually with LET, and this is also suggestive that the coupling reaction between the silyl and alkyl radicals has been actually enhanced with the density of the species distributed linearly along the particle trajectory.

The effects of the molecular weight distribution on the radiation-induced gelation of a real polymer system were considered by Saito [19] and Inokuti [20], who traced the changes in distribution due to simultaneous reactions of main-chain scission and cross-linking analytically. However, in the present case, the molecular weight distributions of the target polymers are reasonably well controlled to be less than $\text{PDI} = 1.2$, and the initial distributions are predicted not to play a major role in gelation. The simultaneous change in the molecular weight distribution due to radiation-induced reactions also results in a nonlinearity of Eqs. (2.1) and (2.2). Therefore, the following equations are proposed to extend the validity of the relationship by introducing a deductive distribution function of molecular weight on the basis of an arbitrary distribution [21]:

$$s + s^{1/2} = p/q + \frac{(2 - p/q)(D_V - D_g)}{(D_V - D)} \quad (2.7)$$

$$D_V = 4 \left(\frac{1}{uu_n} - \frac{1}{u_w} \right) / 3q \quad (2.8)$$

where D_g is the gelation dose, and u is the degree of polymerization (u_n and u_w are initial number-averaged and weight-averaged degree of polymerization, respectively). Equation (2.7) provides a better fit to the observed values of s at high doses than Eq. (2.1). However, the $G(x)$ derived from this fit are almost identical to those in Table 2.1, depending on the molecular weight, because the values are estimated in the low-dose region where Eq. (2.1) is sufficiently linear.

Statistical analysis of the effects of molecular weight distribution was successful partially, and well taken into accounts reaching actual yield of the chemical reaction induced not only by conventional but also by high LET radiations, in reality, high LET radiation-induced changes in molecular weight distribution was in an irrational way and opened for questions as shown in Fig. 2.3 [22]. The degradation reactions by H^+ particles (low LET particles) were traced in a typical way, with gradual shift of molecular weight distribution maxima toward the lower region and the broadenings. In contrast, the changes in the molecular weight distribution upon irradiation to high LET radiations changes exceptionally, projecting a new peak with 100-fold molecular weight range, and the initial peak was unchanged. This is suggestive that, as illustrated in Fig. 2.1, the cross-linking reactions occur only in the limited spatial area around a particle trajectory, and the polymers at the outer area remains unchanged.

During the last century, the concept of spatially limited field of chemical reactions in an ion track; “chemical core” or “chemical track” had been confirmed, visualized, and used in terms of the “damaged area” by the chemical reactions [1, 2, 23, 24]. The size of the field was limited within a few nm spaces, which

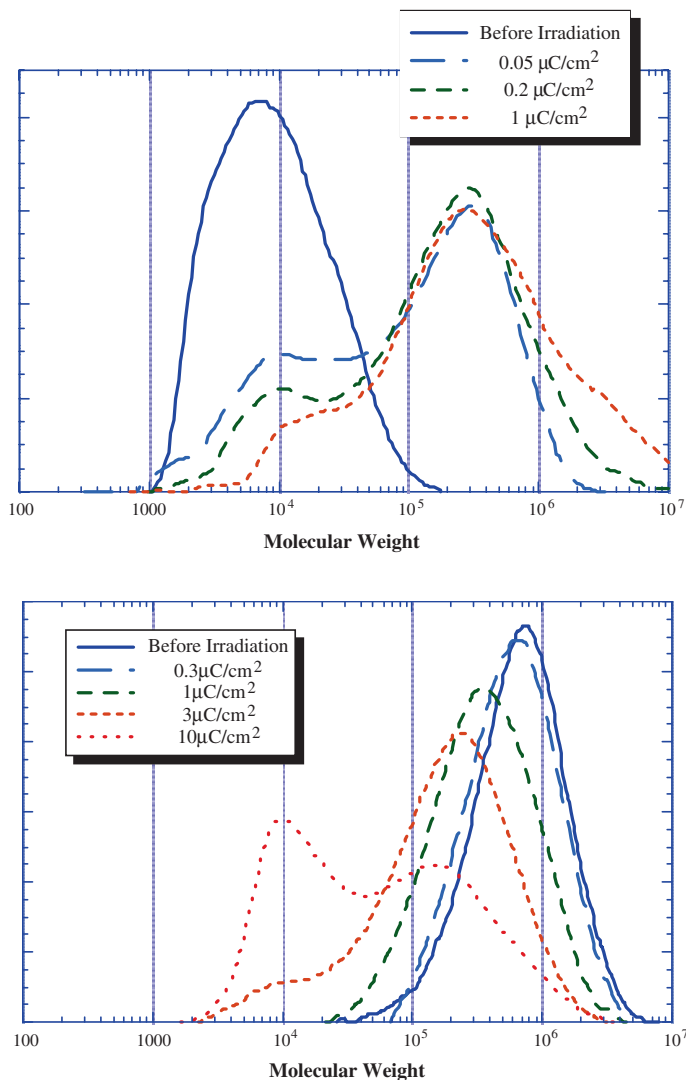


Fig. 2.3 Normalized molecular weight distribution of poly(di-*n*-hexylsilane) (PDHS) with an irradiation to 2 MeV $^4\text{He}^+$ and 20 MeV H^+ ion beams at 295 K. Reprinted with permission from Seki et al. 1997. ©1997, Elsevier (Ref. [22])

was the best fit to the strong demands to the nanomaterials, especially nanowires, nanorods, nanothreds, nanostrings, etc., overall one-dimensional nanostructures with high aspect ratio. Motivated from the demands, the “reactions in an ion track” were designed to produce directly the materials with functions in the twenty-first century as introduced in the following sections.

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