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Gamma-ray induced crosslinking of polynorbornene and its copolymer containing a stabilizing group

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Summary

The gamma-ray induced, solid state crosslinking of polynorbornene(PolyNB) and its copolymer was studied. PolyNB degradates when irradiated in air, but it is readily crosslinked in vacuum. Homopolymer and copolymers containing a stabilizing group, 3,5-di-*tert*-butyl-4-hydroxybenzoyloxy group, were resistant to crosslinking showing induction periods before crosslinking. The irradiated PolyNB showed an ESR signal due to the allyl radical, and the polymer containing the hydroxybenzoyloxy group showed a signal due to the quinolic radical.

Introduction.

Polynorbornene(PolyNB) is a commercially available sulfur vulcanizable rubber. It is not difficult to prepare various functionalized norbornenes having groups with hetero atoms, such as esters, hydroxyl group, etc. Polymerization of such monomers has recently been facilitated by employing new types of metathesis catalysts, such as molybdenum and tungsten alkylidene complexes[1,2], and rutenium and osmium catalysts[3,4] which are more tolerant towards hetero atom-containing functional groups. The incorporation of functional groups into polyalkenamers offers possiblities of obtaining various new materials such as membranes for gas separation, host polymers for liquid crystals, materials with nonlinear optical properties, etc. For example, Lee et al.[5] have reported some electroluminescent PolyNBs. The present authors have previously reported a PolyNB containing 3,5-di*tert*-butyl-4-hydroxybenzoyl group[6,7] and fluorescein[8]. PolyNB is a highly transparent, amorphous polymer, and its use as a host polymer for functional organic compounds is an interesting topic. In such case it is desirable to crosslink the functionalized PolyNBs in order to avoid the host-guest separation and melting, and to increase mechanical strengths. In this work, PolyNB and its copolymers with a NB containing a stabilizer group, 5-{[(3,5-di-*t*-butyl-4-hydroxybenzoyl)oxy] methyl}-2-norbornene (BHBN), were irradiated with γ-ray and their crosslinking behavior was investigated.

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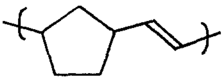
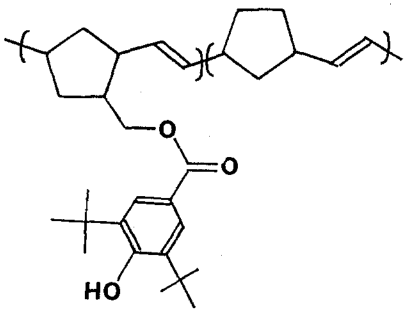
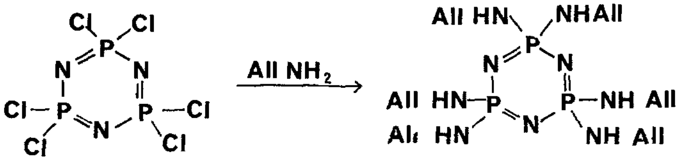
Experimental

PolyNB and its copolymers with BHBN were prepared by the method reported previously[6,7] using $RuCl_3\ xH_2O$ as a catalyst.. Their chemical formula are shown below:





2,2,4,4,6,6-Hexakisallylaminocyclotriphosphazatriene(HAAP) was synthesized by the reaction of the hexachloro compound with allylamine:



The molecular weights were determined by GPC using a Varian Model 9012 with TSK-Gel GMH-6 colum, using THF as solvent. The number average molecular weights of PolyNB, polyBHBN and poly(BN-*co*-BHBN) { d[BN]/d[BHBN] = 11.5},were 4.65, 2.20 and 4.06 x 10^5, respectively, with polydispersities of about 2.

The polymers were made into films by casting of toluene solutions. The films were placed in Pyrex tubes and the tubes were sealed under vacuum. They were irradiated using a Gammer-Beam 651PT Co^{60} with 17000 curies with an intesity of 6.7 kGy/h. The gel percentages were determined from the insoluble fractions after extracting the benzene soluble fractions for 50 hrs using a Soxhlet extractor.

The radiochemical yields of crosslinking(G_c) and of degradation(G_d) were calculated according to the Charlesby-Pinner equation[9]:

$$S + \sqrt{S} = p/q + 1/q\,\mu_1\,r \qquad (1)$$

where S is soluble fraction after irradiation, r is radiation dose in Mrads, q is the proportion of crosslinked units, p is the ratio of number of main chain scission to the total number of polymer chains, and μ_1 is the number average degree of polymerization. By plotting $S + \sqrt{S}$ against 1/r gives $1/q\ \mu_1$ as the slope and p/q as the intercept. The value of G_c is then calculated by the equation[9];

$$G_c = 0.48 \times 10^6\ q/w \qquad (2)$$

where *w* is the molecular weight of monomer unit. The values of G_d were found to be zero indicating that degradation was absent in all systems.

The dose of incipient gel, r_g, was obtained graphically by plotting the gel percentage against irradiation dose, and extrapolating the curve to the zero percentage. The values of r_g were also obtained by plotting $S + \sqrt{S}$ against 1/r of equation (1). The values of 1/r when $S + \sqrt{S}$ is 2, correspond to $1/r_g$[9].

Results and Discussion.

The results of irradiation of the 4 polymeric systems are summarized in Fig. 1. It can be seen that PolyNB readily undergoes crosslinking by γ-irradiation in vacuum. PolyBHBN on the other hand showed an induction period of more than 90 hrs before crosslinking, and the copolymer had about 30 hrs induction period. It is obvious that the phenoxy groups retard crosslinking. It is generally known that aromatic groups retard radiochemical reactions due to absorption of radiation energy. In the case of PolyBHBN, the phenoxy groups provide hydrogen atoms to the allyl radicals formed by the gamma-irradiation.

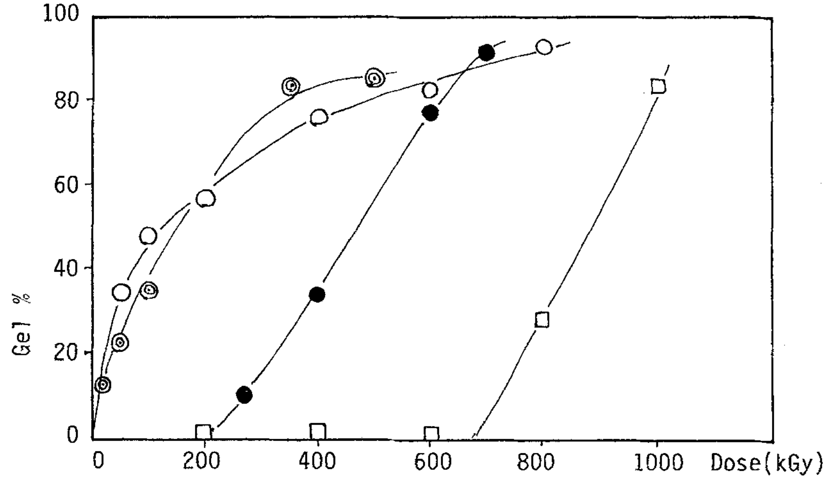
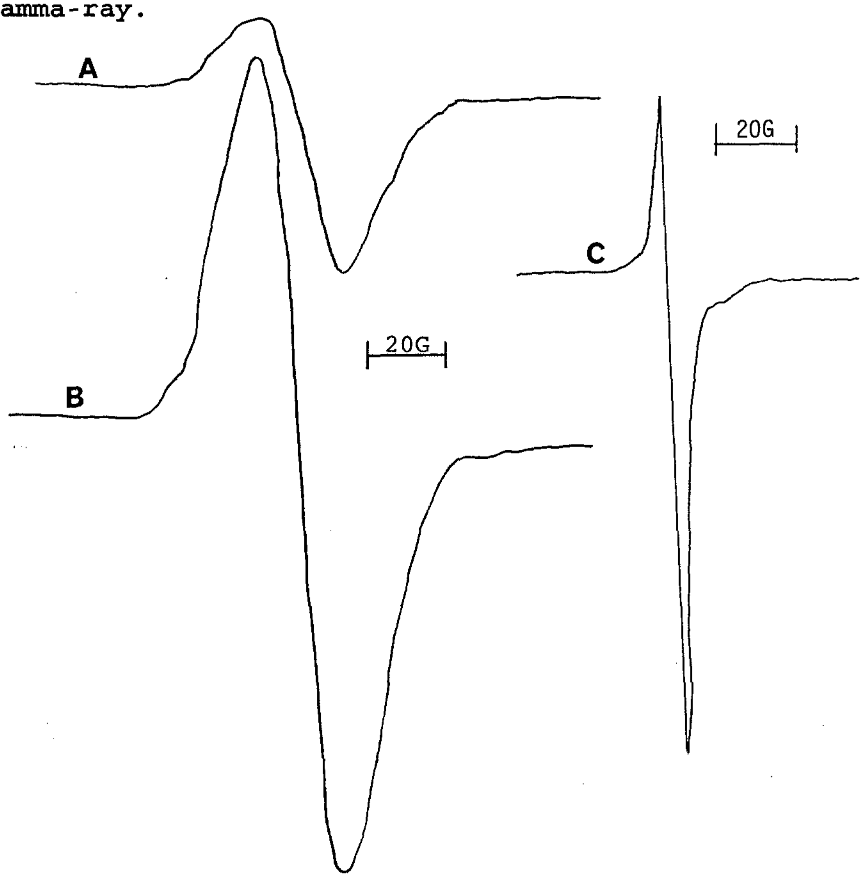


Fig.1.Crosslinking by gamma-irradiation in vacuum.
Intensity=6.7 kGy/h. O:PolyNB, ◎:polyNB+HAAP, □:PolyBHBN, ●:Poly(NB-co-BHBN).

ESR spectra of PolyNB and polyBHBN irradiated with 50 Mrads are shown in Fig. 2. The signal of irradiated polyNB is attributed to the allyl radical[I], and that of polyBHBN is due to the carbon radical[III]. The *g* value of 2.00331 oberved for the irradiated polyBHBN indicates that the radical is not the phenoxy radical[II] but a carbon radical. The radical concentrations for these two samples were found to be 1.36×10^{18} and 3.05×10^{17} for [I] and [III], respectively. These values are considered to be quite high and indicate that reaction (2) readily takes place and that polyNB is a readily crosslinkable polymer by radiation under inert atmosphere.

Fig. 2. ESR Spectra of PolyNB and PolyBHBN Irradiated by Gamma-ray.



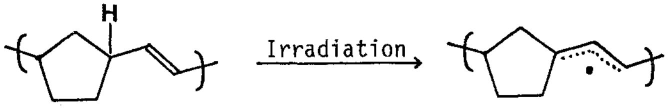
A: PolyNB irradiated with a dose of 430 kGy. Modulation frequency(MF): 100 kHz, Modulation amplitude(MA): 0.08G, Receiver gain(RG): 25. Microwave frequency(MF): 9.12 GHz. ΔH_{pp}=22.82G, g=2.00492. Radical concentration(RC)=7.41 x 10^{16} rad/g.
B: PolyNB irradiated with a dose of 500 kGy. MF : 100kHz, MA: 1.0G, RG: 5.0, MF: 9.13 GHz. ΔH_{pp}=23.5 G, g=2.00492. RC=1.36 x 10^{18} rad/g.
C: PolyBHBN irradiated with a dose of 500kGy. MF: 100kHz, MA: 0.079, R.G: 1.0G, MF: 9.12 GHz, ΔH_{pp}=4.03, g=2.00331. RC=3.05 x 10^{17} rad/g.

Table 1 shows G_c and r_g values for the four systems. The effect of HAAP is not clearly observed in Fig. 1, but the values of radiochemical yield for crosslinking, G_c, and of the dose of incipient gel formation, r_g, indicated that addition of 4 % HAAP accelerated crosslinking appreciably.

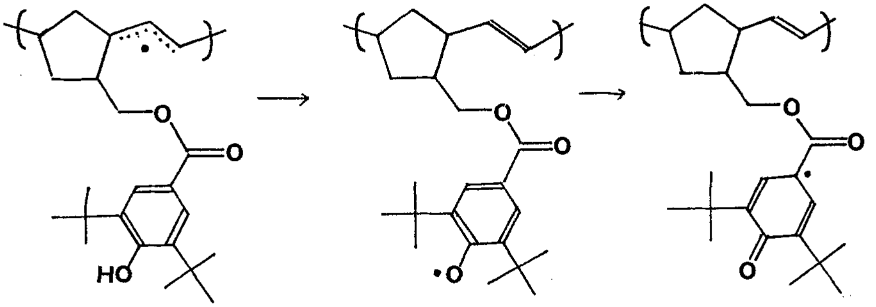
The average molecular weight between crosslinks, M_c, was calculated using the following equation[9] proposed by Charlesby;

$$M_c = 0.48 \times 10^6 / G_c\, r \qquad (3)$$

where r is irradiated dose in Mrad (1 Mrad = 10 kGy). The results are shown in



[I]



[II] [III]

Table 1. Radiochemical yields of crosslinking(G_c) and the doses of incipient gel(r_g) of the polynorbornenes irradiated with gamma-ray with a radiation intensity of 6.7 kGy/h(1Mrad=10kGy) in vacuum.

POLYMERS	Gc	r_g (kGy)
PolyNB	0.21	24.0
PolyNB + 4%HAAP	0.48	10.6
PolyBHBN	0.012	750.0
Poly(NB-co-BHBN)	0.025	234.0

Table 2. It can be seen that in the cases of PolyNB and polyNB with HAAP, crosslinking starts immediately and M_c decreases with increase in radiation dose.

Table 2. Average molecular weight between crosslinking points.

DOSE kGy	PolyNB	PolyNB+HAAP	PolyBHBN	Poly(NB-co-BHBN)
0	936,000	936,000	545,000	813,000
100	228,600	100,000	—	—
400	119,000	26,600	—	480,000
600	38,000	16,600	—	320,000
800	28,600	12,500	500,000	192,000
1000	2,300	1,000	400,000	192,000

It was also found from these results that HAAP accelerated appreciably the crosslinking of polyNB. In the cases of polyBHBN and its copolymer, the crosslinking density is much less than that of polyNB due to the interaction of the stabilizer group.

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