RADIATION YIELD AND RADICALS PRODUCED IN IRRADIATED POLY (BUTYLENE SUCCINATE)

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ABSTRACT

RADIATION YIELD AND RADICALS PRODUCED IN IRRADIATED POLY(BUTYLENE SUCCINATE). The main chemical effects of ionizing irradiation on polymers are crosslinking and chain scission. Both processes occur simultaneously and their yields determine the final results of processing. The radiation yield of crosslinking could be determined by several methods depending on the characteristics of the material and properties of the gel. Radiation parameters of gelation, such as gelation dose and ratio of scission yield to crosslinking yield, as well as their values were estimated. In this study, those parameters depend on the amount of Trimethallyl isocyanurate (TMAIC) in Poly(butylene succinate) (PBS), molecular weight of PBS, and irradiation condition. In the absence of TMAIC, higher molecular weight of PBS required less energy to start gelation process compared to lower molecular weight of PBS. While in the presence of TMAIC all of the PBS samples require similar energy to start gelation process. The existence of macroradicals were observed by Electron Spin Resonance measurements. The result showed that the spectra consisted of signals derived from radicals on carbon nearby carbonyl, and signals derived from radicals on carbon reside between two similar carbon on polymer, both of radicals lead to crosslinking.

Key Words: Poly(butylene succinate); Trimethallyl isocyanurate; Radiation Crosslinking; Radical.

INTRODUCTION

Radiation yield of crosslinking and scission

The ability of polymer to crosslink or to degrade by irradiation is determined by the yield value (G). The yield value (G) is a number of molecule alterations, e.g., crosslink bonds (Gc) or scission acts (Gs) per 100 eV of the absorbed energy [1, 2].

The radiation yield of crosslinking can be determined by several methods depending on the characteristics of the material and properties of the gel [3]. These methods include measurement of:

1. Change of the molecular weight of the polymer before reaching the gel-point,
2. Sol-gel fraction,
3. Gelation-dose value,
4. Swelling equilibrium and
5. Modulus of elasticity.

The main chemical effects of ionizing irradiation on polymers are crosslinking and chain scission. Both processes occur simultaneously and their yields determine the final results of processing [4].

If the crosslinking predominates, an insoluble macroscopic gel will be formed. The sol-gel analysis allows estimating parameters of the process. The effect of chain crosslinking and scission on irradiation was analyzed by Chapiro [4]. Charlesby and Pinner [2] established a simple empirical formula for polymers, where scission and crosslinking occurs randomly. The formula links soluble fraction $s$ with irradiation dose $D$:

$$s + \sqrt{s} = \frac{p_0}{q_0} + \frac{2}{q_0 U_{2,0}} D$$

(1)

where $p_0$ is degradation density (Average number of main chain scissions per monomer unit and per unit dose); $q_0$ is crosslinking density (Proportion of monomer units crosslinked per unit dose); $U_{2,0}$ is the initial weight (Average degree of polymerization), and $D$ is the absorbed dose.

However, this empirical formula was limited to calculations based on processing of polymer having the most probable molecular weight distribution. Deviations of the distribution from the random one affect calculated yield values. Hence, several theoretical modifications of Charlesby-Pinner equation have been attempted, but no simple mathematical expression have been developed [5,6]. Another approach, to avoid an inaccuracy resulted from unknown molecular weight distribution of used polymers, has been proposed by Rosiak et al [7]. The equation (2) allows calculation of radiation parameters of linear polymers of any initial weight distribution, as well as is applicable to the systems, in which an initial material is monomer or branched polymer. After the estimation of gelation dose, $D_g$, the radiation yield of scission and crosslinking can be calculated using equations (3) and (4)

$$s + \sqrt{s} = \frac{p_0}{q_0} + \left(2 - \frac{p_0}{q_0}\right) \frac{D_v + D_g}{D_v + D}$$

(2)

$$G(x) = \frac{4.8 \times 10^5}{M_{w0} \times D_g}$$

(3)

$$G(s)/G(x) = 2p_0/q_0$$

(4)
where $s$ is sol fraction, $G(x)$ and $G(s)$ are the yields of crosslinking and scission, respectively; $D_v$ is the virtual dose, a dose required to change the distribution of molecular weight of the certain polymer in such a way that the relation between weight-average and number-average molecular weight would be equal to 2. The physical states of the polymer, e.g. crystallinity, presence of solutes such as crosslinkers, etc., which may have the influence on the yields, are taken into consideration in this formula, namely in the value of $D_v$ [8,9]. For the polymer, which has random molecular weight distribution ($M_w/M_n = 2$), $D_v$ becomes zero and the Charlesby-Rosiak equation falls into Charlesby-Pinner equation.

**Free radical initiation reaction of PBS1 in the presence of TMAIC**

Exposure of poly(butylene succinate) to high energy irradiation causes crosslinking. Generally, formation of a crosslink requires the presence of two neighbouring radicals, one on each polymer chain [10]. It is postulated that in solid polymers radicals can move and decay slowly. Such mobility can be achieved by a series of hydrogen abstraction and addition reactions. Assuming a random distribution of crosslinks, the doses required for the formation of a crosslink network can be readily evaluated.

A different situation arises when crosslinks occur via a chain reaction, involving both polymer and monomer. An example is the curing of unsaturated polyester/styrene mixtures. Here, the initiation of a chain reaction via a single radical allows a number of crosslinks to occur in a sequence. The crosslinks are therefore no longer distributed at random, furthermore, the dose requirements are considerably reduced. For this purpose one double bond per monomer unit is needed to propagate the chain and in addition one double bond per crosslink to allow the growing polymer chain to attach itself to the polyester. This extra double bond can either occur in the monomer or the polymer chain. Thus the average overall number of unsaturated groups per monomer reacted must exceed unity. Not only the dose requirements are considerably reduced, but also the relationship between solubility and crosslinked density is greatly modified.

Electron spin resonance studies may be expected to provide further information on the intermediates and help to elucidate the nature of the reaction. The aim of the study is to observe the effects of TMAIC on the radiation crosslinking of PBS.
MATERIALS AND METHOD

Materials

Some properties of PBS samples used in this study are shown in Table 1. These polymers were produced at Showa High Polymer Co. Ltd., Japan.

Table 1 Some properties of PBS samples used in this work

| Sample type | Mw      | Mw/Mn | Melting point (°C) | Density (g/cm³) | ∆H (J/g) |
|-------------|---------|-------|--------------------|-----------------|----------|
| PBS1 (Poly(butylene succinate co adipate)) | 2.96 x 10⁵ | 2.00  | 92                 | 1.23           | 45       |
| PBS2 (Poly(butylene succinate co adipate)) | 1.56 x 10⁵ | 1.62  | 93                 | 1.23           | 44       |
| PBS3 (Poly(butylene succinate)) | 1.75 x 10⁵ | 1.80  | 114                | 1.26           | 72       |

Radiation parameters of gelation

The gelation dose and the ratio of scission to crosslinking densities (p0/q0) were estimated by sol-gel analysis and calculated using Charlesby-Pinner equation (1) since the relation between weight-average and number-average molecular weight are equal to 2, with the aid of specially designed computer program [11]. The amount of insoluble fraction (gel) was used to determine soluble part (sol). Yields of crosslinking and degradation were calculated using equations (3) and (4).

ESR measurements

Polymer samples in the form of sheet with dimension 3 x 0.5 x 30 mm and polyfunctional monomer in the form of powder were subjected to drying and evacuation of air for at least 24 hours prior to being sealed in 5 mm diameter of ESR quartz tubes. The irradiation was conducted under vacuum, 10⁻³ Pa at liquid nitrogen temperature, 77 K by γ-rays at the dose rate of 10kGy/h, the sample was irradiated with dose of 20 kGy (The dose of 20 kGy is an effective dose, which the gel has been formed at such dose).

The measurements were performed using a JEOL (JM-FE3) X-band spectrometer with 9.07 – 9.22 GHz frequency, at liquid nitrogen conditions and several temperatures above 77 K.
RESULTS AND DISCUSSION

Yields of radiation processing

Results of radiation processing of PBS with different TMAIC concentrations are shown in Table 2. Degradation to crosslinking density \( p_0/\bar{q}_0 \) is the parameter that allows the determination of the final results of irradiation and is equal to half of the scission yield / crosslinking yield ratio \( [0.5 \times G(s)/G(x), \text{equation} \ (4)] \). The lower \( p_0/\bar{q}_0 \) value indicates more efficient crosslinking. Table 2 shows that radiation yield of crosslinking of PBS containing 1% TMAIC is the most effective for crosslinking among samples of various TMAIC concentration.

Table 2. Comparison of gelation dose \( D_g^a \), degradation to crosslinking density \( p_0/\bar{q}_0^b \), crosslinking \( G(x)^b \) and scission \( G(s)^b \) yields of Poly(butylene succinate) irradiated by Electron Beam (2 MeV, 1 mA) in vacuum plastic bag at a dose rate of 10 kGy/sec.

| %TMAIC | \( D_g^a \) | \( p_0/\bar{q}_0^b \) | \( G(x)^b \) | \( G(s)^b \) |
|--------|------------|----------------|-------------|-------------|
| PBS1   |            |                |             |             |
| 0      | 33.25      | 1.17           | 0.05        | 0.11        |
| 0.2    | 3.03       | 0.93           | 0.54        | 0.99        |
| 0.5    | 3.82       | 0.65           | 0.58        | 0.75        |
| 1.0    | 5.66       | 0.46           | 0.53        | 0.48        |
| 2      | 8.42       | 0.35           | 0.19        | 0.14        |
| 3      | 9.57       | 0.40           | 0.17        | 0.14        |
| PBS2   |            |                |             |             |
| 0      | 95.89      | 0.93           | 0.03        | 0.05        |
| 0.5    | 4.26       | 0.99           | 0.64        | 1.28        |
| 1.0    | 6.62       | 0.74           | 0.41        | 0.61        |
| 3.0    | 11.56      | 0.73           | 0.24        | 0.35        |
| PBS3   |            |                |             |             |
| 0      | 40.49      | 1.24           | 0.08        | 0.19        |
| 0.5    | 2.27       | 0.83           | 1.36        | 2.25        |
| 1.0    | 4.67       | 0.63           | 0.66        | 0.83        |
| 3.0    | 10.19      | 0.47           | 0.30        | 0.28        |

\( ^a \) Gelation doses were determined by gel-sol analysis.

\( ^b \) values calculated by Charlesby-pinner equation (1), and equations (3) and (4).
The gelation dose (a minimum required energy to start gelation process) of PBS without TMAIC, appeared lowest for PBS1 compare to PBS2 and PBS 3 (Fig. 1). It is due to higher molecular weight of PBS1. It can be postulated that PBS1 requires less energy to start produce gel compare to PBS2 and PBS3. The molecular weight has an impact on the gelation behavior. The gelation dose is the lowest, which means that the high molecular weight at similar dose facilities gelation. In contrast for PBS1 containing TMAIC the molecular weight has no effect in gelation dose, as can be seen from Fig. 1 that the gelation dose is almost similar for all of the PBS samples used in this study. However the last product (gel fraction) depends on degradation to crosslinking density (p₀/q₀). It can be seen from table 1 that PBS1 has lower p₀/q₀ than that of PBS2 and PBS3, for any amount of TMAIC contents. It can be deducted that the polymer with higher molecular weight gives lower p₀/q₀, which means higher yield of gel formation.

![Figure 1. Gelation dose versus TMAIC concentration of PBS.](image)

**Radicals generated on PBS1 and TMAIC**

The ESR spectra of PBS1 irradiated at 77 K and measured at various temperatures are shown in Fig. 2. The effect of temperature on ESR signal was studied over the temperature range of 77-323 K. It can be seen that all spectra contain overlap coarse signal at central part of the signals. At 77 K the signals revealed triplet as dominant signal overlap with quintet as weak signals. By annealing up to 203 K the quintet signal reveals apparently, the spectrum showed that the radicals decayed rapidly by annealing upon 203 K. There are no essential changes of the signal up to 323 K.
The signals measured at 77 K show triplet with a splitting constant 1.2 mT, it is most likely result from radical being produced by proton abstraction from carbon located nearby carbonyl (I). By annealing up to 203 K, the quintet signal reveals apparently, with β proton splitting constant 1.7 mT and α proton splitting constant 0.6 mT as a result from radical occurred at carbon reside between two similar carbon (II).

Figure 2. ESR spectrum of irradiated PBS1 at various temperatures from 77 K to 323 K (γ dose of 20 kGy, in Vacuum).

Figure 3. ESR spectrum of irradiated TMAIC at various temperatures from 77 K to 323 K (γ dose of 20 kGy, in Vacuum).
The ESR spectra of TMAIC irradiated at 77 K and measured at various temperatures are shown in Fig. 3. It can be seen as in Fig. 2. All spectra contain overlap coarse signal at central part of the signals. The ESR spectra do not change substantially on heating from 77 K to 298 K. However, on further heating, the spectra of the ESR signal changes significantly. The spectrum becomes weak as the radicals decay. It can be seen that the radicals decay slightly when the sample was annealed at 323 K.

At 77 K the signals revealed as the results from an overlapping of two radicals, the triplet and doublet spectrum. The triplet spectrum with a splitting constant 2.3 mT is most likely the result from radical (III) being produced by proton abstraction from methyl groups. The doublet spectrum with a splitting constant 1.5 mT is a result from radical (IV) being produced by proton abstraction from carbon nearby nitrogen on cyclic structure. It was observed that the ESR signal for TMAIC decayed somewhat slower than that for PBS1.

Matsumoto [12] reported that the high reactivity of growing polymer radical formed from unconjugated monomer such as TMAIC promotes the methallylic hydrogen abstraction. Other monomers such as methyl methacrylate, MMA and methacrylonitrile, which also contain allylic C-H bonds, do not undergo extensive degradative chain transfer, thus forming
high-molecular-weight polymers. This is ascribed to lower reactivity of the propagating radicals from conjugated monomers [13].

The ESR spectra of PBS1 containing 1% TMAIC irradiated at 77 K and measured at various temperatures are shown in Figures 4. The results are similar with the ESR spectra for PBS1 without TMAIC. It is due to the PBS1 mixed sample contents only small amount of TMAIC, thus the TMAIC signal is not apparent in the figure. The signals measured at 77 K show triplet with a splitting constant 1.2 mT, the splitting constant is similar with the signals of pure PBS1. It results from radical being produced by proton abstraction from carbon located nearby carbonyl (I). By annealing up to 203 K, the quintet signal appears strongly, with β proton splitting constant 1.7 mT and α proton splitting constant 0.6 mT as a result from radical occurred at carbon reside between two similar carbon (II). This result is also similar with the spectra of pure PBS1.

There are several paths available for the attachment of TMAIC to the PBS1 chains. Fig. 5 shows the chemical structure of crosslinking of PBS1. High proportion of the pendant methallyl groups would be converted to methallyl radicals by irradiation. These methallyl radicals could abstract proton from the PBS1 chains to effectively increase the G value for PBS1 radical production and subsequently the G (crosslinking). The pendant methallyl double bonds of TMAIC may react with free radicals on adjacent PBS1 chains, resulting crosslinking of the chains.
Figure 5. Crosslinking of PBS1.

Model of radiation-induced formation of crosslinking in PBS in the presence of polyfunctional monomer is shown in Fig. 6. It can be seen that the monomer took place as a bridge between the polymer chains in the amorphous parts.

Figure 6. Model of radiation-induced formation of crosslinks in PBS in the presence of polyfunctional monomer.
CONCLUSION

In the absence of TMAIC, PBS1 requires less energy to start gelation process compare to PBS2 and PBS3. While in the presence of TMAIC all of the PBS samples require similar energy to start gelation process.

ESR spectra of irradiated PBS1 and PBS1 containing 1% TMAIC at dose of 20 kGy showed similar results, it can be deduced as two different radical, both of radicals lead to crosslink each other. For PBS1 containing 1% TMAIC, the TMAIC spectra cannot be seen. It is due to the small amount of TMAIC in PBS1, thus the spectra of TMAIC were not apparent in the figure.

The radicals in TMAIC decayed slower by increasing temperature than that of radical in PBS1 or PBS1 containing 1% TMAIC.

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