

## 《Original》 A Study on the Preparation of Wood-Plastic Combinations(Ⅱ). Monomer Impregnations and Gamma-ray Induced Polymerizations

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### Abstract

A study on the preparation of wood-plastic combinations by gamma-ray induced polymerization is carried out.

In monomer impregnation, the rates and amounts are determined for various woods. The polymerization rates of various monomers and monomer mixtures impregnated mainly domestic woods are studied varying the total gamma-dose and gamma-dose rates.

The obtained data indicate that: 1) in impregnation of monomer, populus deltoides is the fastest in rate, and the most impregnated in amount 2) the general trends of polymerization of monomers in woods is in the order of vinyl acetate--methyl metacrylate--styrene, ranging from 3 to 15 Mrad of total dose in rate of  $4 \times 10^4$  rad/hr., thus vinyl acetate or methyl metacrylate is suitable monomer in view of polymerization rate, 3) the successful woods in combination with monomer are pinus rigida and pinus densiflora in view of polymerization rate, 4) the monomers in woods are more easily polymerized under the conditions of moderately lower dose rate,  $2.1 \times 10^4$  rad/hr.

### 요 약

감마선 중합에 의한 목재와 플라스틱의 복합체 제조에 있어서, 각종 목재들에 대한 단량체의 침투량과 침투속도를 검토하였으며, 중합에 있어서는 국산 목재를 주로하여 이에 각종 단량체 및 그 혼합물, 방사선의 조사량, 조사율, 이에 따르는 중합속도등을 검토하여 다음과 같은 결과를 얻었다.

1) 단량체 침투에 있어서, 침투속도나 침투량은 모두 포플라에서 컸다.

2) 복재내에서의 단량체의 중합속도는 비닐 아세테이트-메틸메타아크릴레이트-스타이렌의 순서이며 필요한 전 조사량은 조사율  $4 \times 10^4$  rad/hr에서 3~15 Mrad의 범위였다. 따라서 중합속도의 관점에서 볼때 비닐아세테이트나 메틸메타아크릴레이트가 좋은 단량체이다.

3) 단량체와의 결합에 있어서 리기다송, 육송등이 중합속도로 보아 효과적인 목재이다.

4) 목재 내부에서 단량체는 비교적 낮은 조사율인  $2.1 \times 10^4$  rad/hr에서 더 용이하게 중합되었다.

## 1. Introduction

After the first application of radiation polymerization technique to the monomers impregnated into wood<sup>1)</sup>, extensive studies on the preparation of wood-plastic combinations are being continued. Kenaga<sup>2)</sup>, and Karpov<sup>3-5)</sup> studied on the wood-plastic combinations using gamma-ray, almost simultaneously, and many other investigators such as Hodgins<sup>6, 7)</sup>, Kent<sup>8-13)</sup> and Siau<sup>14)</sup> contributed very much to the study on this field.

Since 1965, in particular, the study on the preparation of W.P.C. using thermal curing method, instead of using radiation, has also started. Even though the product W.P.C., obtained by the thermal curing method is not much different in properties from that of the product obtained by radiation<sup>15)</sup>, the radiation curing is still better method in view of the following advantages;

1) handling of monomers is simple since no catalyzer is mixed with monomer for use in radiation polymerization,

2) easiness in control of polymerization rate, especially in large scale practices,

3) easiness in prevention of monomer evaporation during polymerization reaction since it is carried out in ordinary atmospheric pressure and room temperature,

4) the produced W.P.C. is much purer than that of the thermally cured, and will show no corrosion and no degradation of wood cellulose after W.P.C. is made since there is not any catalyzer in the W.P.C. product.

In view of these advantages, the radiation curing method is preferential to the thermal curing, in both of the preparation study and industrial application, even if much more investigation is required for installation of gamma-irradiation facilities. Continuing the first report<sup>16)</sup> we have studied in this paper if some of the domestic woods and imported

lans can be made practically to useful W.P.C. or not, in situ of impregnation of available monomers and subsequent gamma-ray induced polymerizations; measurement of the impregnation rates and impregnation amounts of monomers into various woods as well as the measurement of polymerization rates of the impregnated various monomers or monomer mixtures varying the total dose, dose rates and wood species are main objects of present study in practical preparation aspects.

## 2. Experimental

### 1) Materials and Instruments

#### a) Wood samples:

Wood samples are prepared as same way as the method described in our first paper on this study.

#### b) Monomers:

i) Styrene; technical grade is purified as following; monomer is mixed with 15% sodium hydroxide solution in 4:1 volume ratio and vigorously agitated to remove the stabilizers such as p-tertiary butyl catechol or hydroquinone. After removing the aqueous layer, the monomer is washed twice with distilled water and dried with calcium chloride. Thus the stock solution in refrigerator is made. When required, this is distilled under reduced pressure.

ii) Methyl metacrylate(M. M. A.); technical grade is washed with saturated solution of sodium hydrogen sulfite by mixing 10:1 volume ratio. Again washed with 5% sodium hydroxide solution, mixing 10:1 volume ratio to remove stabilizer. After separation of the monomer layer from the aqueous, it was washed with plenty of distilled water repeatedly, and subsequently dried with calcium chloride, filtered, and distilled.

iii) Vinyl acetate; to the 5 parts of technical grade monomer 1 part of 10% sodium acetate solution is vigorously mixed and the aqueous

layer is separated removing the stabilizer. Then purified in usual way.

c) Radiation source:

The  $^{60}\text{Co}$  gamma source, around 500 Ci, installed in our institute is used after intense measurements of dose rate by chemical dosimetry.

**2) Preparation of W.P.C.**

a) Selection of sample coating material:

According to up-to-date knowledge in treatment of impregnated wood samples for irradiation, wrapping method using aluminum foil or polyethylene sheet and/or encapsulation in aluminum boxes are applied. Since this method is very troublesome and costly, we have tried to coat the impregnated surfaces with some water-soluble polymer materials such as polyvinylalcohol (P.V.A.) or gelatine instead of wrapping and encapsulating the samples. Impregnated wood samples and control samples are coated using either 15% P.V.A. solution or 8% gelatine solution, or wrapping in ordinary way with aluminum foil, and then weighed. These samples are irradiated under constant dose rate of  $2.0 \times 10^5$  rad/hr. for 5 days, and eventually reweighed. The variation in weight of wood samples are shown on Table 1.

In the estimation of weight variations, correction are made using the data obtained from the control samples which are not impregnated with the monomer.

b) Measurement of impregnation rate:

Variously sized wood samples are made; *ie*, 5 cm in tangential direction to the annual ring, 5cm in normal direction to the annual ring and 5, 10, 15 or 20 cm in height, respectively. The sample surfaces which are formed from the directions of tangential or normal to the annual ring are coated twice with the selected coating material; *ie*, 15% P.V.A. solution. To the styrene monomer, 0.2% of hydroquinone is added to prevent probable polymer-

ization during impregnation experiment, and further added slight amount of methyl red dye to visualize the front line of the monomer ascending.

To keep constant conditions through out this experiment, all wood samples are submerged into the monomer in same depth, 2 cm, from the bottom end, standing in vertical direction. The least time required to run the monomer from the bottom end to the upper is read for each sample. (Fig.1). Further, to measure the amount of monomer impregnated in different duration of soaking, following experiments are also carried out; the wood samples are prepared in size of 1 cm<sup>2</sup>, vertical to the center run of annual ring, and 10 cm, parallel to the center run of the annual ring. These samples are put into the vacuum desiccator and evacuated to remove air, moisture and other vaporizables siezed in the cavities of wood samples. The loaded monomer in dropping funnel connected to the desiccator is slowly poured into the desiccator paying special attention to prevent air-entering. When the wood samples are completely submerged into monomer, slow stream of nitrogen gas is applied to equilibrate the pressure in the desiccator with the atmosphere. Then this setting is allowed to uptake monomer for 24 hr or so. In definite time interval, the samples are taken out, and weighed. The impregnated amount of monomer is calculated in weight % of wood. (Fig.2 and Fig.3) The same methods are applied in the impregnation of monomer-mixtures.

c) The effect of total dose on polymerization % in wood-polystyrene combinations:

The polymerization % of styrene in various wood were measured under constant dose rate,  $4.56 \times 10^4$  rad/hr, but varying total dose. The impregnated wood samples are weighed and irradiated. The irradiated samples are then put into a vacuum desiccator and fully evacuated to remove unpolymerized monomer or

even oligomer. The increased weight are expressed as polymerization % in the wood when the sample shows constant weight. (Fig. 4).

d) The effect of total dose on the polymerization % in pinus densiflora-plastic combinations:

Pinus densiflora samples impregnated with various monomer were coated with P. V. A. film according to the aforesaid method, and irradiated under constant dose rate,  $4.0 \times 10^4$  rad/hr. but varying total dose. After irradiation, the same treatments were done as 2), c). (Fig. 5).

e) The effect of total dose on the polymerization % in combination of wood with polymer mixture:

Different monomers were mixed by 1:1 volume ratio and then treated it just like the single monomer. Experiments were carried out in the same way as 2), c). (Fig. 6-8).

f) The effect of dose rate on the polymerization % in wood-polystyrene combinations:

The polymerization % were measured under the constant total dose, 10 Mrad, but varying dose rate;  $2.13 \times 10^5$ ,  $4.56 \times 10^4$  rad/hr etc.

### 3. Results and Discussion

According to the data on table 1. gelatine is not a suitable coating material for monomer impregnated wood samples. This is owing to the fact that the coating is hardly made homogeneous with gelatine solution. On the other hand, P. V. A. coated samples showed slight increases in weight. This is due mainly to the absorption of moisture by the coated P. V. A. film during irradiation. When subtracted the weight increase of the control sample, 0.045, from the weight increases of the others the net increases of weight are merely -0.007gr., -0.011gr, and -0.030 gr respectively. These values are negligible comparing the values resulted from the other methods. Thus, it is confirmed that the P. V. A. coating method is a valuable means for W. P. C. preparations.

In the measurement of impregnation rate, populus deltoides is the fastest among the wood samples. (Fig. 1.). It will be attributable to the fact that there is less amount of resin in the central part of wood comparing with the other part. Actually, the monomer reaches to the upper end earlier in central area and much

Table 1. Weight variations of styrene-impregnated wood samples depending coating or wrapping methods

coating or wrapping materials		weight (g) of wood	weight (g) after impreg.	weight (g) after coat'g	weight (g) after irr.	weight variation during irr. (g)
P. V. A.	1	2.650	6.206	6.423	6.461	0.038*
	2	2.683	6.339	6.592	6.626	0.034*
	3	2.669	6.319	6.524	6.539	0.015*
	4	2.662	—	3.362	3.407	0.045*
gelatine	1	2.696	6.123	7.355	7.134	0.221*
	2	2.544	5.770	7.457	6.980	0.495**
	3	2.515	5.797	6.927	6.792	0.135**
	4	2.403	—	6.475	6.163	0.312**
Al foil	1	2.408	5.990	—	5.960	0.030**
	2	2.341	5.990	—	5.841	0.059**
	3	2.476	5.959	—	5.947	0.012**
	4	2.490	—	—	2.490	0.000

\* incr ease.

\*\* decrease

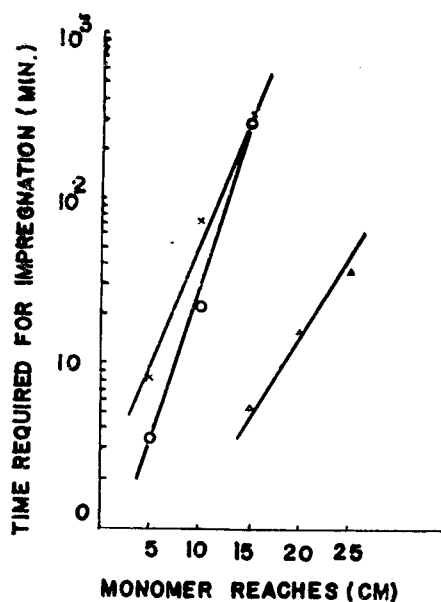


Fig. 1. Impregnation rate of styrene for various wood samples under atmospheric condition

×: pinus densiflora, ○: pinus rigida,  
Δ: populus deltoides

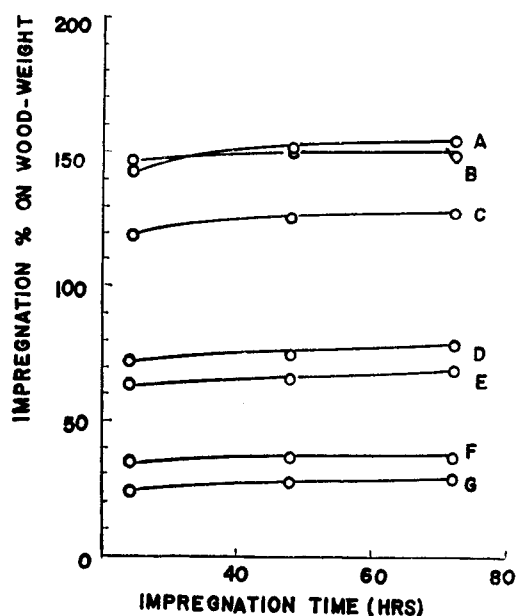


Fig. 2. Impregnated % versus impregnation time for Styrene monomer on the vacuum process

A: populus deltoides, B: pinus densiflora  
C: pinus rigida, D: white lauan,  
E: yellow lauan, F: apitong,  
G: red lauan

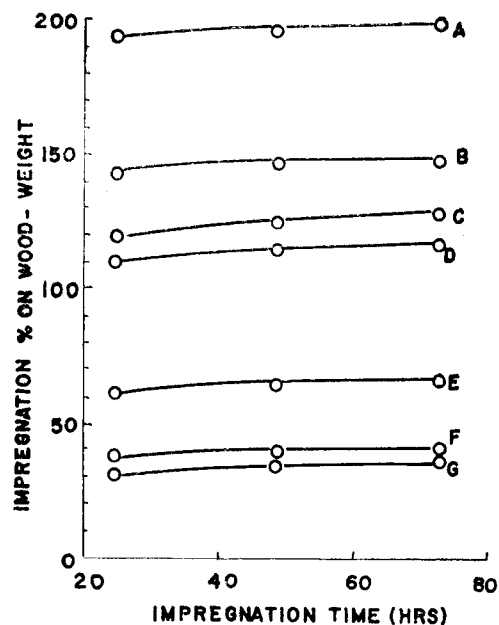


Fig. 3. Impregnation % versus impregnation time for vinylacetate monomer on the vacuum process

A: populus deltoides, B: pinus densiflora,  
C: pinus rigida, D: white lauan,  
E: yellow lauan, F: apitong,  
G: red lauan

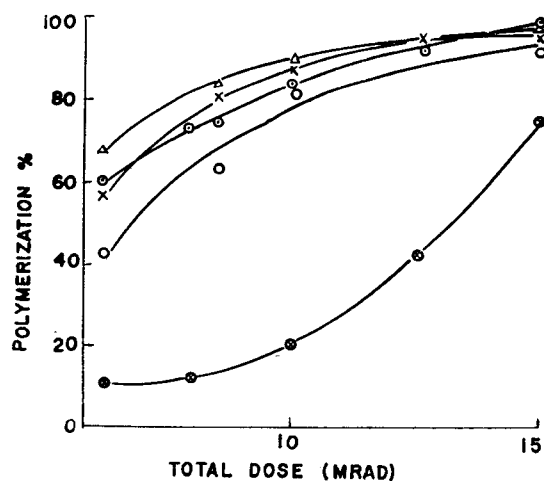


Fig. 4. Dependence of polymerization % on total gamma-dose in wood-polystyrene combinations

Δ: pinus densiflora, ×: populus deltoides  
⊙: white lauan, ○: yellow lauan,  
⊗: apitong

afterwards in outer area of the cross section of the wood stock.

In general, it takes very long time to uptake monomers under atmospheric pressure without any penetration aid. For acceleration, the wood samples should be contained in a tight vessel and evacuated, submerged into monomer, and then pressed on the monomer.

The data obtained from the measurement of impregnated amounts of monomer (Fig. 2 and Fig. 3) indicate that red lauan and apitong are hardly impregnated. In contrast, pinus densiflora and populus deltoides are easily impregnated with the monomers showing 150~200% on weight bases (Fig. 2, Fig. 3). It is believed that the differences in the amount impregnated are closely related to the contents of resin and to the different densities of wood cellulose.

The effect of total dose on the polymerization % in the wood-polystyrene combination was investigated at constant dose rate as  $4.56 \times 10^4$  rad/hr. Under this condition the total dose of about 10 Mrad is required, in average, to get 80% polymerization, except in case of apitong. (Fig. 4). The styrene monomer in apitong polymerize only 20% under 10 Mrad irradiation. This fact suggest that the natural born hard wood is relatively difficult to impregnate with monomer, and even if impregnated, it is still difficult to polymerize.

The effect of total dose on the polymerization % of various monomer in pinus densiflora is shown in Fig. 5. For 100% polymerization, styrene needs 15 Mrad, while vinyl acetate and methyl metacrylate need 3 and 4 Mrad, respectively. This result almost coincides with the well known fact that the polymerization rate is closely related to the G values of monomers in the initial irradiation stage. It is also reported that the polymerization rate of M. M. A. monomer in various wood is depend upon dose rate<sup>17)</sup>; the polymerization is com-

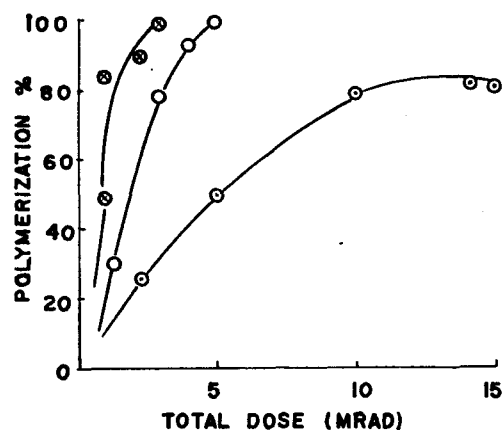


Fig. 5. Polymerization % of various monomers in pinus densiflora as a function of total dose

⊗: vinylacetate ○: M. M. A., ⊙: styrene

pleted in 3 Mrad of dose with the dose rate of 10 rad/sec., but in 6 Mrad of dose with the dose rate of 30 rad/sec. 10 rad/sec and 30 rad/sec are equivalent to 0.36 Mrad/hr and 0.108 Mrad/hr, respectively. On the other hand, the total dose of 4 Mrad was sufficient with the dose rate of 0.04 Mrad/hr for 100% polymerization of M. M. A. in our experiment. The slight differences of total dose are often encountered in many literatures. It is also reported in afore-cited literature<sup>17)</sup> that M. M. A. in maple tree or white pine is completely polymerized under the dose rate of 20 rad/sec and the total dose of 5-6 Mrad.

It is encouraging to find that pinus densiflora, the most abundant wood in this country, will be made to W.P.C. by impregnating vinyl acetate or M. M. A. monomer and subsequent irradiation of 3-4 Mrad gamma ray, relatively small amount of total dose. The vinyl acetate and M. M. A. are both easily polymerizable monomers in wood by radiation induced polymerization. Styrene monomer needs more dose to bring about considerable polymerization. However, the polymerizability order of vinyl acetate--M. M. A.--styrene is not to be expected in case of catalyzed polymerization.

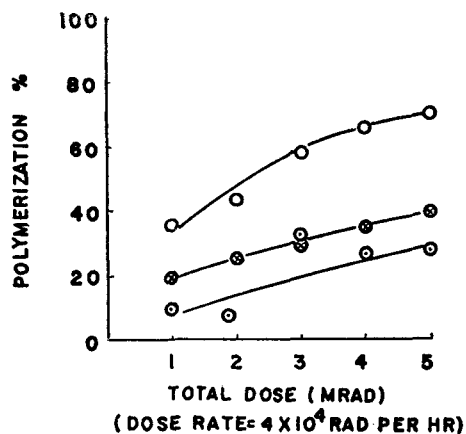


Fig. 6. Polymerization % of impregnated monomer-mixture as a function of total dose

○: pinus rigida, ⊗: pinus densiflora,  
 ⊙: populus deltoides  
 monomer-mixture; styrene+vinylacetate=50:50, in volume

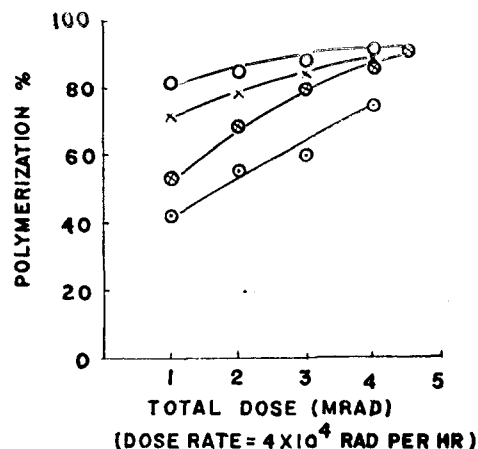


Fig. 8. Polymerization % of impregnated monomer-mixture as a function of total dose

○: pinus rigida, ×: white lauan,  
 ⊗: pinus densiflora, ⊙: populus deltoides  
 monomer-mixture; vinylacetate+M. M. A.  
 =50:50, in Volume

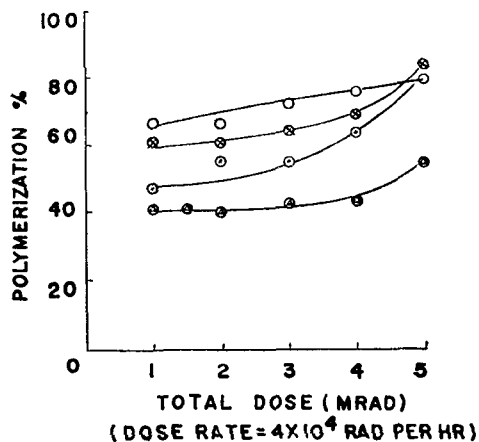


Fig. 7. Polymerization % of impregnated monomer-mixture as a function of total dose

○: pinus rigida, ⊗: white lauan,  
 ⊙: pinus densiflora, △: populus deltoides  
 monomer-mixture; styrene+M. M. A. =50:50, in volume

The mixture of styrene and vinyl acetate (1:1 in volume) uptaken in pinus rigida shows relatively high polymerization rate comparing that in populus deltoides. (Fig. 6). The similar result is obtained with the monomer mixture of styrene and M. M. A. uptaken in the same two woods. (Fig. 7). In both cases polymeri-

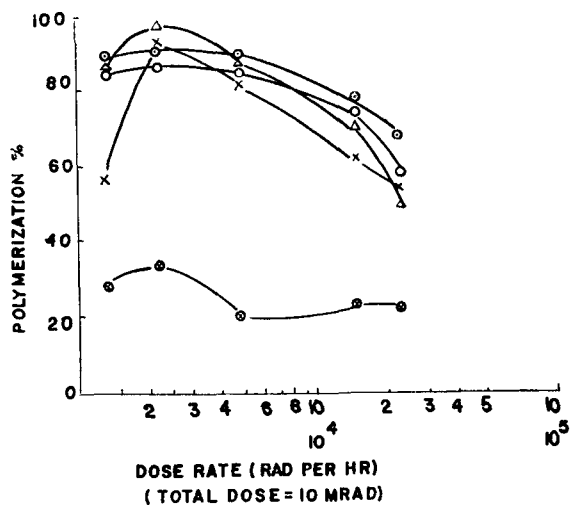


Fig. 9. Polymerization % of impregnated styrene monomer as a function of dose-rate

⊙: pinus densiflora, ○: white lauan,  
 ×: yellow lauan, △: pinus deltoides  
 ⊗: Apitong

zation rates are generally poor, because a component of the mixture is styrene which is not easily polymerized. With the readily polymerizable monomer mixture, composed of vinyl acetate and M. M. A., the polymerization

rate is so fast that it is polymerized nearly 90% within 5 Mrad of total dose. (Fig. 8). Even though the average polymerization % is higher than that in the cases of the former two, still the polymerization % in populus deltoides is relatively low.

As Fig. 9 shows, in the fixed total dose (10 Mrad), the effective polymerization is accomplished under moderately low dose rate,  $2.1 \times 10^4$  rad/hr regardless of the wood species. The results thus obtained coincide well with that in the literature<sup>17)</sup>.

#### 4. Conclusion

1. In the impregnation of monomers, populus deltoides is the fastest, and the most impregnated.

2. P.V.A. coating method is confirmed as a useful method in treatment of impregnated wood samples.

3. The promising monomers for preparation of W.P.C. are vinyl acetate and M.M.A. in view of polymerization rate in wood.

4. The successful woods are pinus rigida pinus densiflora in view of polymerization rates.

5. The monomer or monomer mixture uptaken in apitong need more total dose than those uptaken in other woods.

6. The polymerization rate is faster in irradiation with moderately lower dose rate,  $2.1 \times 10^4$  rad/hr, than in irradiation with higher one.

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