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Radiation polymerization of *N*-vinylcarbazole and electroluminescent behavior of poly(*N*-vinylcarbazole)

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Abstract

Radiation polymerization of *N*-vinylcarbaozle (VCz), in benzene solutions, in vacuum or nitrogen-bubbled at different concentrations was carried out by ^{60}Co γ-ray radiation at a dose rate of 10.5 kGy/h. Unlike other vinyl compounds, VCz polymerizes at a higher radiation dosage; however, the side groups of carbazole are not eliminated from their sites. Gel permeation chromatography was used to characterize molecular weight and distribution. Oxidation was found only when polymerization was conducted using nitrogen-bubbled solutions at lower concentration of VCz. The optimization to polymerize VCz was obtained based on the dependence of polymer yield on radiation dosage. Single layer electroluminescent device based on commercially radically polymerized poly(*N*-vinylcarbazole) shows inferiority in luminance and efficiency, due to electronic traps resulted from heterogeneous end groups, when compared with that based on radiation-polymerized PVCz free of heterogeneous end groups. The effect of the different end groups may be confirmed by the divergent morphology when PVCz thin films were annealed above glass transition temperature (T_g). © 2000 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Polymerization; *N*-vinylcarbazole; Electroluminescence

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1. Introduction

Poly(*N*-vinylcarbazole) (PVCz) is a kind of photoconductive polymer [1–3]. Judging from the structure of its monomer, *N*-vinylcarbazole (VCz), it has been proved that the electronegative nitrogen withdraws electrons from the double bond via an inductive effect. On the other hand, unshared electrons in N donate to the double bond by p–π conjugation to create an electron-rich double bond. The latter effect dominates in the course of competition between induction and conjugation effects. Accordingly VCz can be polymerized cationically but not anionically. Cationic polymerization were studied extensively with catalysts such as protonic acid, Lewis acid, metal salts and organic cation salts, as described in detail elsewhere [4].

It was reported in the earlier literature [5] that colored PVCz could be prepared by thermal polymerization from its monomer, but the results showed bad reproducibility.

Almost colorless and high molecular-weight PVCz can been obtained by radical polymerization [6] based on AIBN initiator. Charge-transfer polymerization [7] of VCz was reported as early as 1963. Solid-state radiation polymerization [8] was conducted in the 1960s from monomer crystals.

Radiation polymerization can be called “clean polymerization”, since only external high-energy radiation is exposed on the monomer so that no further impurity will be included. Initiator moieties remain at the end sides for the cases of polymerization by active species such as radical, anionic and cationic polymerizations so that electronic traps, due to heterogeneity between the end groups and main chains, may be induced if used as photoconductive materials whose performance will be deteriorated as a consequence [2].

PVCz as a hole-transporting material has been used widely in electroluminescent (EL) devices [9–12]. Single-layer device [9] based on PVCz doped by a novel coumarin derivative has been fabricated. The EL emission peak varies from 445 to 472 nm, depending on the ratio of PVCz to the doping dye. Two-layer devices [10–12] have been mostly adopted so as to tune the color of EL emission. Two-layer device consisting of a hole-transporting PVCz layer and 8-hydroxyquinoline aluminum (Alq)-emitting layer showed maximum EL at 2300 cd/m^2.

In this study, radiation polymerization was carried out in benzene solutions, as benzene is a well known

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Table 1
Composition of VCz solutions in benzene

Solution	Concentration[a]
A	0.25
B	0.5
C	1.0

[a] VCz (g) in solvent (ml).

radiation-resistant material, because of its unique π-electron delocation.

PVCz, free of electronic traps, was prepared thus far by radiation polymerization in benzene solutions in vacuum. EL behavior based on either radiation-polymerized or commercially radically polymerized PVCz were compared herein.

2. Experimental

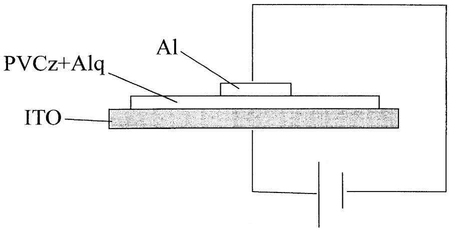
2.1. Materials

The initial solutions with the compositions as listed in Table 1 were prepared. Glass tubes containing 2 ml of the above solutions were connected with vacuum gauge at 77 K to evacuate air. They were then sealed under the pressure of 10^{-3} Pa and subjected to ^{60}Co γ-ray radiation at room temperature at a dose rate of 10.5 kGy/h. Vials containing the above solutions were bubbled by nitrogen to replace air atmosphere. After being capped, they were irradiated by ^{60}Co γ-ray at the same rate. VCz and benzene, purchased from Tokyo Chemical Industry Co. Ltd (Japan), were used without further purification.

2.2. Gel permeation chromatography

Gel permeation chromatography (GPC) was performed on a TOSO TSK-Gel super high molecular-weight column in tetrahydrofuran (THF) as an eluent at a flowing rate of 0.4 ml/min at 40°C under the pressure of 20 kg/m^2 with a UV detector at 254 nm.

A droplet or small piece of gel-like specimen irradiated for different dosages was spread on glass slides to evaporate benzene at room temperature. In some cases, e.g. gel-like specimens, it is necessary to evaporate benzene at 50°C. THF solutions of the dried products at the concentration of 0.5–1 mg/ml were made for the GPC measurements.



Scheme 1.

2.3. Electroluminescent device

Either commercially radically polymerized or radiation-polymerized PVCz (1.5 g) and 0.4 g Tris(8-quinolinolato) Alq were dissolved in 100 ml dichloroethane and stirred until a unique greenish yellow solution was obtained. Commercially radically polymerized PVCz, Alq and dichloroethane were products of Tokyo Chemical Industry Co. Ltd (Japan). They were used as received. For simplicity, EL devices based on commercially radically (C-PVCz) and radiation-polymerized PVCz (R-PVCz) are denoted as devices I and II, respectively, in the later section.

It should be mentioned that the R-PVCz for EL device was prepared from the initial solution C at the dose of 693 kGy. After radiation, the gel-like specimen was dissolved in benzene. Ethanol was used as a nonsolvent to precipitate PVCz. The precipitant was filtered, washed and finally dried in vacuum.

Indium tin oxide (ITO)-coated glass substrates (Products of Casio Co. Ltd, Japan) were cleaned as described in the literature [13].

Oxygen plasma (output = 500 mW) at around 1000 Pa was further conducted to process the pretreated ITO-coated glass substrates to improve the ITO properties [14].

Mixture solutions of PVCz and Alq were coated on the cleaned ITO-coated substrates by dip coating in a clean room. Aluminum electrodes were deposited on thin films by vacuum deposition below 5×10^{-4} Pa. Single-layer EL devices were fabricated as sketched in Scheme 1. The thickness of the single layer for both devices I and II was optimized to be 10 nm. EL behavior was investigated by monitoring the dependence of current density and EL intensity on applied voltage.

3. Results and discussion

Fig. 1 shows GPC diagrams of specimens irradiated for different dosages from initial solutions A, B and C in vacuum. The polymer distribution becomes broader when the radiation dosage increases. For the case of polymerization from the initial solution B, very different macromolecular features prevail; GPC peaks denoting polymeric fractions become complex when radiation dosage increases. It is obvious from the GPC diagrams that there are two shoulders beside the main peak when the radiation dosage is 924 kGy. It is proposed that linear macromolecules become branched so that there are some fractions whose molecular weight becomes higher.

As far as polymerization conducted from the initial solution C is concerned, GPC peaks remain unchanged; however, insolubility due to crosslinking was induced at doses up to 924 kGy. Consequently, GPC measurement could not be carried out.

Neither branching nor crosslinking is observed for the polymerization from the initial solution A.

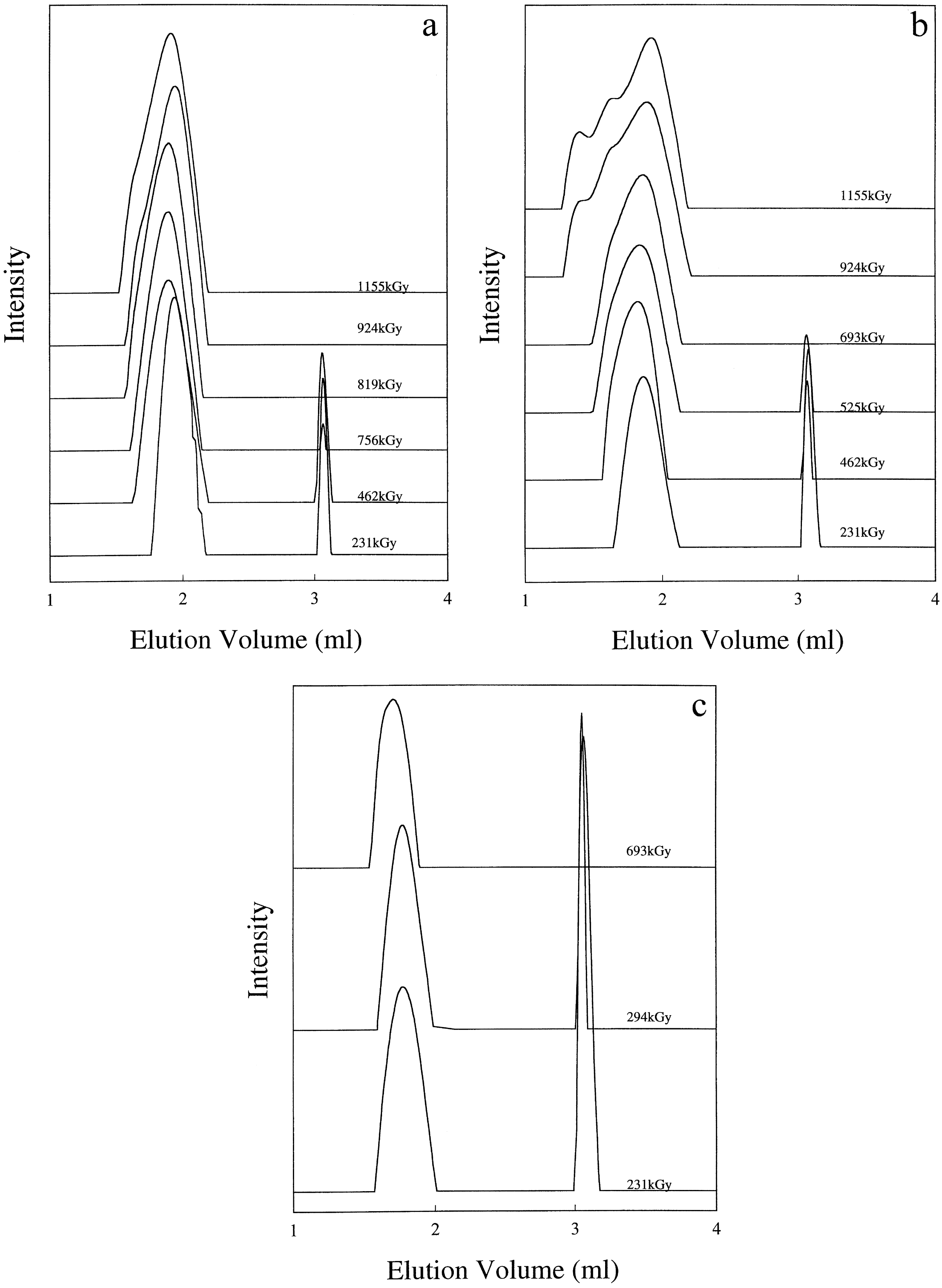


Fig. 1. GPC diagrams of specimens irradiated in vacuum (a, b and c refer to those from the initial solutions A, B and C in turn, so is the case in Fig. 2).

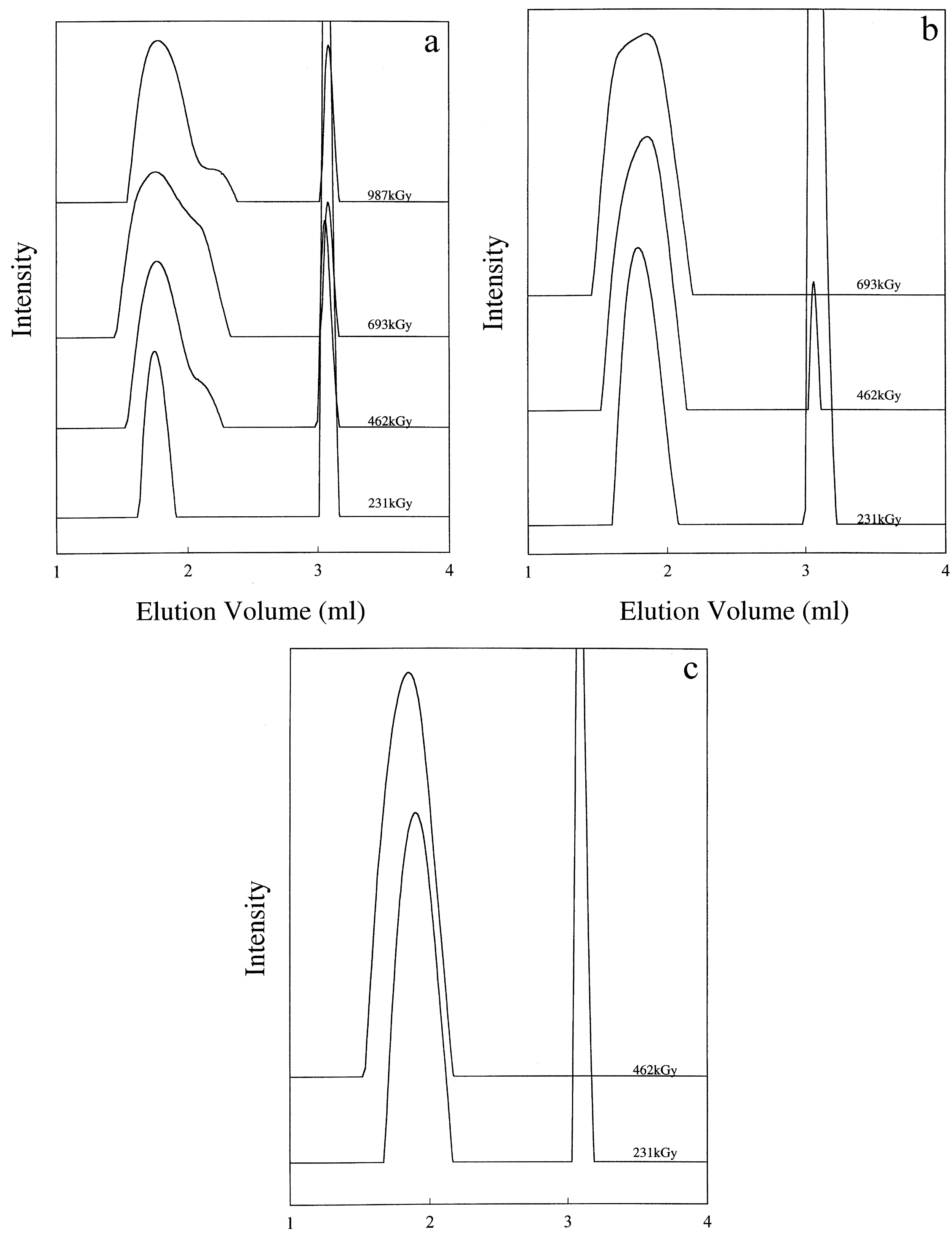


Fig. 2. GPC charts of specimens irradiated from nitrogen-bubbled solutions.

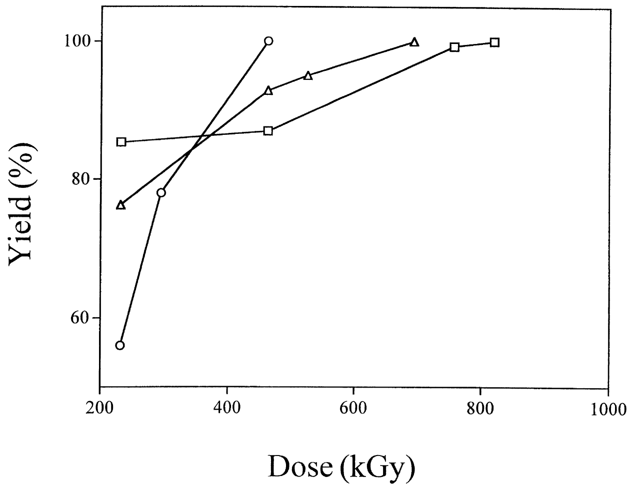


Fig. 3. Dependence of polymer yield on radiation dosage for polymerization in vacuum (□, △ and ○ refer to the polymerization from the initial solutions A, B and C, respectively).

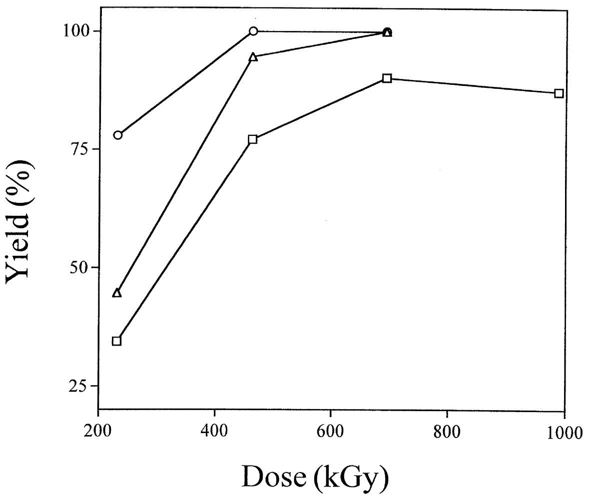


Fig. 4. Relationship between polymer yield and radiation dosage for polymerization from nitrogen-bubbled solutions (the symbols are the same as in Fig. 3).

Only branching is noted, while crosslinking may need a higher dosage exceeding the experimental dosage here, when polymerized from the initial solution B.

For the case of polymerization from the initial solution C, crosslinking is found, while branching could not be detected. It may be inferred that it takes a short time to accomplish the transformation from a linear to a crosslinking polymer when polymerization is conducted from concentrated solutions.

To overview the polymerization of VCz in benzene solution in vacuum, it is noted that polymerization is fulfilled at higher dosage, compared with other vinyl compounds [15] such as (meth)acrylates and vinylpyrrolidone.

It may be questioned whether the carbazole groups might be eliminated from the sites at such a higher dosage. As a matter of fact, X-ray photoelectron spectral (XPS) data, performed on a Perkin–Elmer X-ray photoelectron spectrometer, for PVCz obtained from the initial solutions A and B at 1155 kGy indicated that the ratios of C to N fit the value in Ref. [16]. The results showed that carbazole groups remain at their original sites. Nuclear magnetic resonance spectra of the above cases were consistent with that in the literature [17,18].

For comparison, polymerization of VCz in the initial solutions bubbled by nitrogen was conducted below 693 kGy at the rate of 10.5 kGy/h. GPC diagrams are depicted in Fig. 2. It is noted that a shoulder, which addresses a lower molecular-weight fraction appears when polymerized from the initial solution A at 462 and 693 kGy. It is assumed that oxidation, due to residue oxygen in the bubbled solution, takes place such that peroxide radicals were formed, which could not propagate further into higher molecular weight polymers. Accordingly, the distribution became broader, too. The oxidation has been confirmed by XPS measurement of specimens of the above cases, which showed O1s spectra with binding energy at 532–533 eV, similar to that of poly(ethylene oxide) [16].

If polymerized from the initial solutions B and C, which were also nitrogen-bubbled, oxidation could not be obviously found within the experimental dosages, but polymer distribution becomes broad when radiation dosage goes up, as noted in Fig. 2.

Polymer yield (C_P) can be postulated from the GPC chart by the following equation:

$$C_P = \frac{A_P}{A_P + A_M} \tag{1}$$

where A_P and A_M refer, respectively, to the areas covered by polymer and monomer peaks in GPC diagram.

Judging from Fig. 3, indicating the dependence of polymer yield on radiation dosage, it is seen that polymer yield can reach 100% from the initial solutions A, B and C in vacuum. However, the following sequence addresses the rate of accomplishment of the polymerization: $A < B < C$. It is necessary to further investigate the mechanism of polymerization to explain why at the same dosage (below 300–360 kGy), the polymer yield is lower than the initial solution with higher concentration of VCz, and vice versa. Only after a certain dosage, the polymer yield increases with the initial concentration of VCz at the same dosage.

Table 2
Optimization of polymerization of VCz

Initial solutions	Radiation dosage (kGy)	
	In vacuum	Nitrogen-bubbled
A	> 819	
B	> 693	> 693
C	693–894	> 462

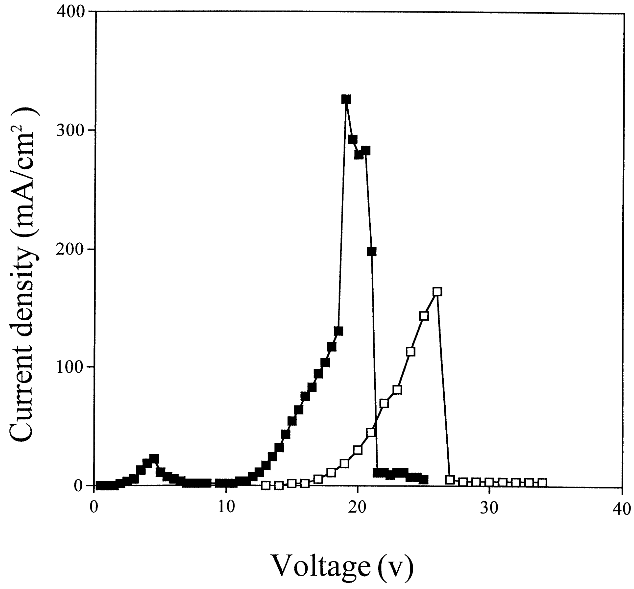


Fig. 5. Dependence of current density on the applied voltage of devices I and II (in Figs.5, 6 and 7, □ and ■ refer to devices I and II, respectively).

In the case of polymerization from nitrogen-bubbled VCz solutions, polymer yield increases with the concentration of VCz in the initial solutions at the same dosage, as illustrated in Fig. 4. Polymer yield could not get 100% from the initial solution A; degradation occurs beyond 693 kGy.

Based on the above results, the optimization for polymerization of VCz has been summarized in Table 2.

Fig. 5 depicts the dependence of current density on the applied voltage of devices I and II. It is noticeable that below 10 V, there is current flow in device I and from 10 V on, its current increases sharply. On the other hand, current in device II began to increase from 13.5 V. Fig. 6 shows the EL intensity versus applied voltage in devices I and II. It indicates that device I showed lower threshold than device II, at 10 and 13.5 V, respectively. Device I has unstable EL intensity at maximum, while EL intensity of device II increases up to 400 cd/m^2 until it is broken at 26 V. Device II is more resistant to higher voltage than device I.

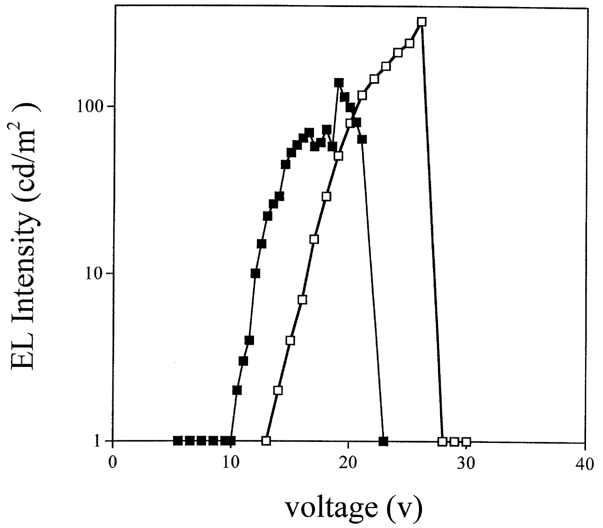


Fig. 6. Plot of EL intensity versus applied voltage in devices I and II.

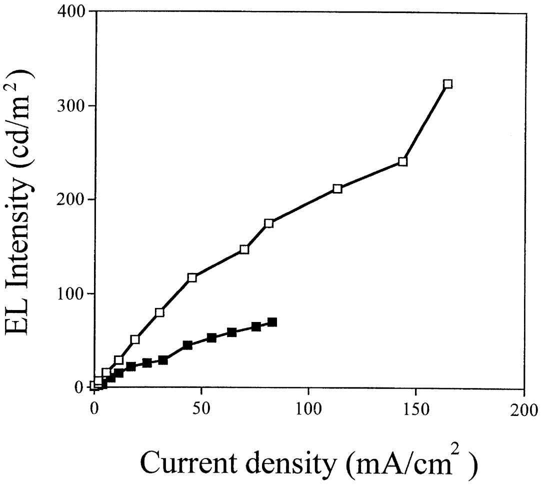


Fig. 7. Relationship between EL intensity and current density for devices I and II.

Judging from Fig. 7, representing the relationship between EL intensity and current density for devices I and II, it can be concluded that the efficiency of device II is higher than that of device I. The reason why the performance of device II is better than that of device I may be due to the difference in the end groups of C- and R-PVCz while the macromolecular weight and distribution keep similar as shown in Fig. 8.

As initiator moieties remain at the ends of main chains of C-PVCz, heterogeneous nucleation for crystallization may take effect when thin films were annealed at 326°C for 1.5 h in nitrogen. The difference in crystallization of thin films of C- an R-PVCz can be seen in Fig. 9: C-PVCz could be crystallized while R-PVCz could not. This may be due to the divergent end groups of PVCz. Heterogeneous end groups in C-PVCz may play the role of electronic traps for EL of device I. As a result, the EL performance deteriorates,

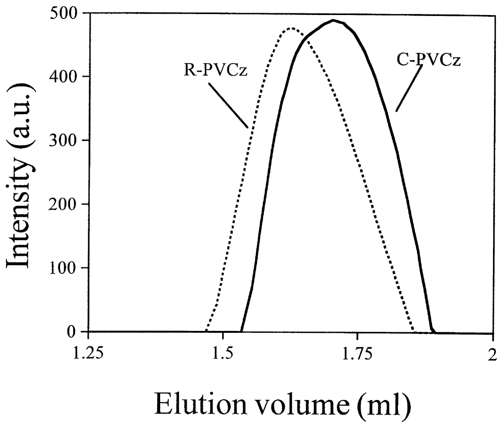


Fig. 8. GPC charts of C- and R-PVCz.

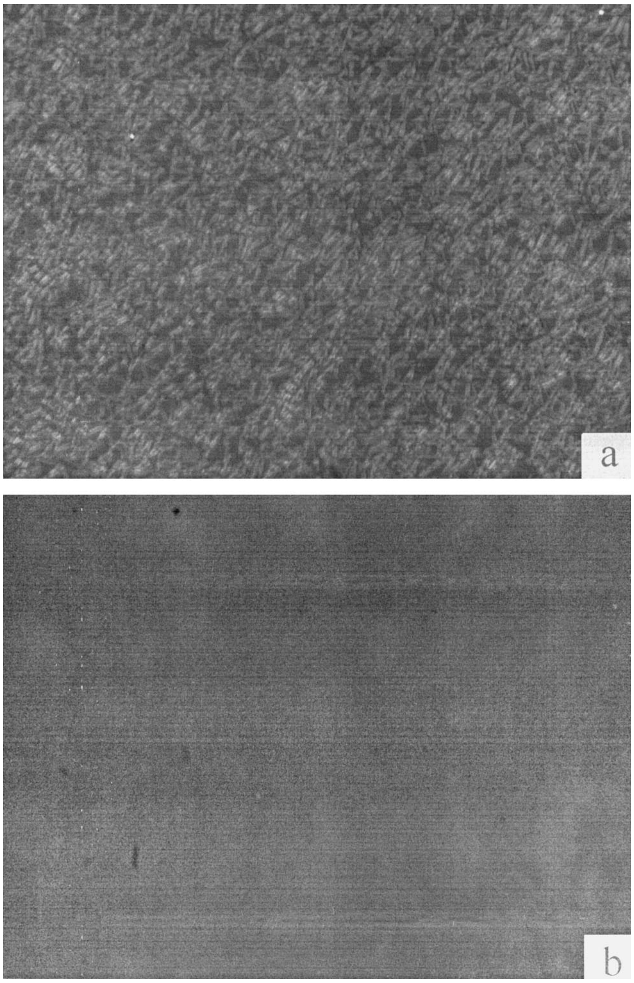


Fig. 9. Morphology of thin films of (a) C-; and (b) R-PVCz annealed at 326°C for 1.5 h in nitrogen.

e.g. earlier current flow and higher current but lower EL intensity after threshold.

4. Conclusion

Radiation polymerization of VCz can be accomplished at higher dosage, but carbazole groups were not removed from their sites, as compared to other vinyl compounds. Optimizations for polymerization of VCz were obtained. The performance of EL devices based on commercially radically polymerized PVCz is inferior to that based on radiation-polymerized PVCz due to radical moieties remaining at the end sites as electronic traps for EL device.

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