

Low-Temperature Photoinitiation Solution Polymerization Behavior of N-Vinylcarbazole in Tetrahydrofuran

Won Seok Lyoo,¹ Han Do Ghim,² Hee-Sam Kim,³ Joon Ho Kim,¹ Sam Soo Kim,¹
Won Sik Yoon,¹ Jinwon Lee,⁴ Sang-Seob Lee⁵

¹School of Textiles, Yeungnam University, Kyongsan 712-749, Korea

²School of Materials Science and Engineering, Seoul National University, Seoul 151-742, Korea

³Department of Textile Design, Korea Textile and Fashion Institute, Taegu 704-901, Korea

⁴Department of Chemical Engineering, Kwangwoon University, Seoul 139-701, Korea

⁵College of Natural Science, Kyonggi University, Suwon 442-760, Korea

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ABSTRACT: N-Vinylcarbazole (VCZ) was solution-polymerized in tetrahydrofuran (THF) at -20 , 0 , and 20°C using the photoinitiation method; the effects of the amount of solvent, polymerization temperature, and photoinitiator concentration were investigated. On the whole, the experimental results corresponded to predicted ones. Low polymerization temperature using photoinitiation proved to be successful in obtaining poly(N-vinylcarbazole) (PVCZ) of a high molecular weight with a smaller temperature rise during polymerization; nevertheless of free radical polymerization by 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN). The photo-solution polymerization rate of VCZ in THF was

proportional to the 0.47 power of ADMVN concentration. The molecular weight was higher and the molecular weight distribution was narrower with PVCZ polymerized at lower temperatures. For PVCZ prepared in THF at -20°C using a photoinitiator concentration of 0.00005 mol/mol of VCZ, a weight-average molecular weight of $510,000$ was obtained, with a polydispersity index of 1.73 , and a degree of lightness converged to about 99% . © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 3667–3672, 2002

Key Words: VCZ; THF; photoinitiation

INTRODUCTION

Poly(N-vinylcarbazole) (PVCZ) has been a major subject of material science because it can be used as a good photo-conductor,^{1–3} charge-transfer complexes,^{1–4} electroluminescent devices,^{5–8} and photo-refractive materials.^{9–13} These can be possible in the form of uniform film, especially a thick film above $100\ \mu\text{m}$ thickness for photo-refractive application. To apply to these fields, it is essential to prepare PVCZ of high molecular weight and high linearity by adopting a new method to polymerize N-vinylcarbazole (VCZ).^{14–16}

Up until now, several methods has been developed for the polymerization of VCZ such as a free radical,^{16–19} conventional cation (protonic acids, Lewis acids, carbocations),^{20–24} photoinitiation,^{25,26} Ziegler-Natta,²⁷ charge transfer,²⁸ electrochemical,^{29,30} vapor deposition,¹⁵ solid state,³¹ etc. Free radical polymerizations of VCZ using azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) as initiators have been performed to prepare PVCZ of a molecular weight of below $100,000$.^{16,18,19} In free radical bulk polymeriza-

tion of VCZ, an increased polymerization rate arising from greater temperature rises at higher polymerization temperature lowered the molecular weight of PVCZ. High molecular weight (HMW) PVCZ is, therefore, hardly obtained by this method. To reduce the latent heat and the viscosity of the medium, free radical solution polymerization of VCZ was conducted. The solution polymerization method has advantages of easy control of viscosity and of higher conversion than those of bulk polymerization. However, frequent chain transfer reactions to monomer makes it unfavorable to obtain HMW PVCZ of superior molecular structure.^{16,18,19} This is more problematic for conventional solution polymerization usually conducted at temperatures above 40°C .

For preparation methods of high-performance PVCZ film by solution casting, the molecular parameters of PVCZ such as molecular weight and its distribution and linearity influence the physical properties of the film. This implies that polymerization conditions may affect structure and properties of PVCZ film because they determine the molecular parameters of PVCZ.

In this study, we utilized low-temperature photoinitiation polymerization³² that is superior to chemical initiation in producing linear HMW PVCZ, owing to a relatively lower propagation rate of polymerization and less probability of termination reaction. That is, to

Correspondence to: Won Seok Lyoo (wslyoo@yu.ac.kr).

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TABLE I
Parameters for Photo-Solution Polymerization of VCZ

Type of photoinitiator	ADMVN
Type of solvent	THF
Photoinitiator concentration	0.00005 mol/mol of VCZ 0.0001 mol/mol of VCZ 0.0002 mol/mol of VCZ 0.0005 mol/mol of VCZ
Monomer concentration	0.25 mol/mol of THF 0.50 mol/mol of THF 0.75 mol/mol of THF
Temperature	-20, 0, 20°C
Radiation type	ultraviolet ray
Radiation source	high-pressure mercury lamp (500 watt)

increase the molecular weight and linearity and to minimize side reactions, VCZ was polymerized in an ultraviolet (UV)-ray initiated solution system at -20, 0, and 20°C. To evaluate the effects of polymerization conditions on the polymerization behavior of VCZ, the kinetic study of the polymerization of VCZ in tetrahydrofuran (THF) initiated by UV-ray has been performed. In addition, the effects of the amount of solvent, polymerization temperature, and photoinitiator concentration on the conversion of VCZ into PVCZ and molecular weight, molecular weight distribution, and lightness of PVCZ polymerized were investigated.

EXPERIMENTAL

Materials

VCZ (Aldrich Co.) was purified by recrystallization from *n*-hexane and dried in vacuum at 30°C for 2 days (melting point = 65.5°C). The photoinitiator 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN)³³⁻³⁵ (Wako Co.) was recrystallized at low temperature twice from absolute methanol. Other extra-pure grade reagents were used without further purification.

Polymerization

VCZ and THF were added in a Pyrex tube, which was placed in a low-temperature methanol bath, and this was flushed with nitrogen for 4 h. After the polymerization temperature was fixed and ADMVN was added, respectively, the mixture was irradiated with a high-pressure 500-W mercury lamp. For comparison with UV initiation results, general nonphoto solution polymerization of VCZ was conducted at 50°C using ADMVN. When polymerization had been completed, the polymer was purified by reprecipitation from the THF/methanol. After the elimination of monomer from the polymerization product in a vacuum had been completed, conversion was calculated by measuring the weight of the polymer. Conversions were

averages of three determinations. Polymerization conditions are listed in Table I.

Characterization

The molecular weight of PVCZ was calculated by eq.(1)³⁶.

$$[\eta] = 1.44 \times 10^{-4} [M_w]^{0.65} \text{ (THF at 25}^\circ\text{C)} \quad (1)$$

where $[\eta]$ and M_w are intrinsic viscosity and weight-average molecular weight, respectively.

The molecular weight distribution and polydispersity index (M_w/M_n) were obtained by gel permeation chromatography (GPC). A Waters' GPC Model 515 was equipped with a bank of four Styragel columns using THF as a solvent. The calculations were based on a calibration curve obtained with 14 polystyrene molecular weight standards with range of 2500–8,500,000 ($M_w = 2500, 4000, 20,000, 35,000, 50,000, 90,000, 200,000, 400,000, 600,000, 1,000,000, 1,920,000, 2,000,000, 4,300,000, 8,500,000$) purchased from Aldrich. The molecular weight of the sample is the polystyrene equivalent molecular weight.

A homogeneous 1.0 g/dL solution of (PVCZ)s in 1,1,2,2-tetrachloroethane were obtained at polymerization temperatures of -20, 0, and 50°C poured onto a stainless steel tray and dried at room temperature to produce films. The lightness of the PVCZ film was measured by Color eye (I.D.I., model C).

RESULTS AND DISCUSSION

Photo-solution polymerization behavior

It has been known that radiation-initiated bulk polymerization might be used for production of HMW polymer with little branching. This method has the following advantages: The radiation initiation rate is temperature-independent. Because the process can be carried out at low temperatures, undesirable side reactions are avoided. The initiation rate can be easily

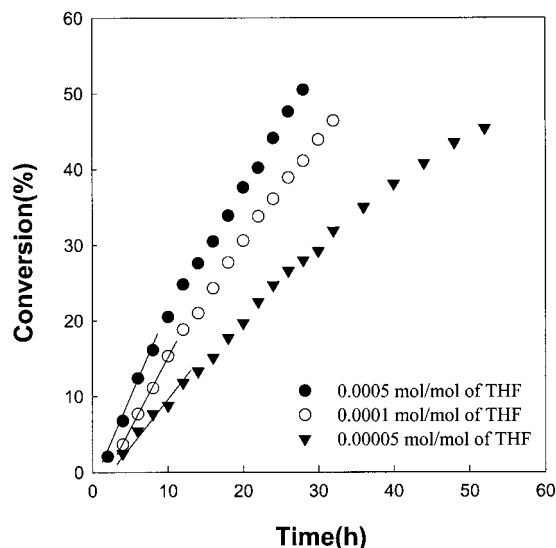


Figure 1 Conversion of VCZ into PVCZ in the early stage of polymerization in THF at -20°C using a VCZ concentration of 0.75 mol/mol of THF with polymerization time.

changed. Therefore, the polymerization rate and molecular weight can be controlled. General photoinitiators used for radical polymerization of vinyl monomers are azo, benzoin, and benzophenone types. Azo and benzoin types are cleavage-type photoinitiators. On the other hand, benzophenone is the hydrogen abstraction type, and it was known that its initiation rate is slower and its initiation mechanism is more complex than those of cleavage-type photoinitiators.³⁷ In this study, to identify the effect of photoinitiator on the molecular weight and conversion of the resultant polymer, we used a low-temperature azo compound, ADMVN, of the formula $\text{R}-\text{N}=\text{N}-\text{R}$ which are decomposed into free radicals by UV-ray.

In the radiation-initiated radical polymerization, the rate of polymerization (R_p) may be expressed by eq.(2),³⁸

$$R_p = k_p (I_0 \phi I \varepsilon / k_t)^{0.5} [M] [I]^{0.5} \quad (2)$$

where I_0 is the incident light intensity, ϕ is a quantum yield, l is a path length, ε is an extinction coefficient of photoinitiator, $[I]$ and $[M]$ are the concentrations of photoinitiator and monomer, and k_p and k_t are reaction rate constants of propagation and termination, respectively. This expression implies that the rate of polymerization is increased with increasing the concentration of photoinitiator. Effect of initiator concentration on the conversion of VCZ into PVCZ prepared in THF at -20°C using a monomer concentration of 0.75 mol/mol of solvent is shown in Figure 1. It was shown that the greater the initiator concentration, the higher the polymerization rate, in agreement with eq.(2).

The dependence of polymerization rate on photoinitiator concentration can be determined by a kinetic

study called initial-rate method.³⁹ Polymerization rate can be expressed by the exponential forms of reaction agents. In the early stage of polymerization the reaction rate coincided with the slope of the conversion-time relation. For small changes in initial concentration of one reagent with the other held constant, the ratio of the polymerization rate can be related to the corresponding ratio of increments. If a measurement is made at two different initial concentrations of one component, the order with respect to that component can be simply determined by using eqs. (3)–(9):

$$- (d[M]_1 / dt) = (R_p)_1 = k[M]_1^{n_1} [I]_1^{n_2} [S]_1^{n_3} \quad (3)$$

$$- (d[M]_2 / dt) = (R_p)_2 = k[M]_2^{n_1} [I]_2^{n_2} [S]_2^{n_3} \quad (4)$$

$$- (d[M]_3 / dt) = (R_p)_3 = k[M]_3^{n_1} [I]_3^{n_2} [S]_3^{n_3} \quad (5)$$

$$(R_p)_1 / (R_p)_2 = ([I]_1 / [I]_2)^{n_{2a}} \quad (6)$$

$$(R_p)_2 / (R_p)_3 = ([I]_2 / [I]_3)^{n_{2b}} \quad (7)$$

$$(R_p)_3 / (R_p)_1 = ([I]_3 / [I]_1)^{n_{2c}} \quad (8)$$

$$n_2 = (n_{2a} + n_{2b} + n_{2c}) / 3 \quad (9)$$

This procedure can be used to determine all exponents like n_1 , n_2 , and n_3 . From the calculation, it was found that the photo-polymerization rate of VCZ in THF at -20°C was proportional to the 0.47 powers of AIBN concentration. That is in good accordance with theoretical prediction by eq. (2).

Figure 2 shows the effect of monomer concentration on the conversion of VCZ into PVCZ polymerized in

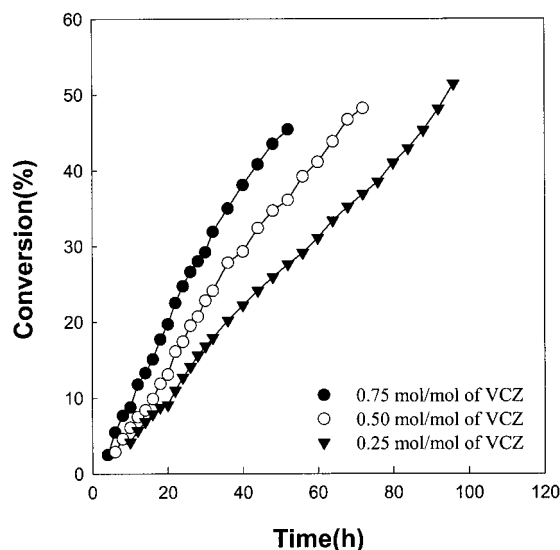


Figure 2 Conversion of VCZ into PVCZ polymerized in THF at -20°C using an ADMVN concentration of 0.00005 mol/mol of VCZ with polymerization time.

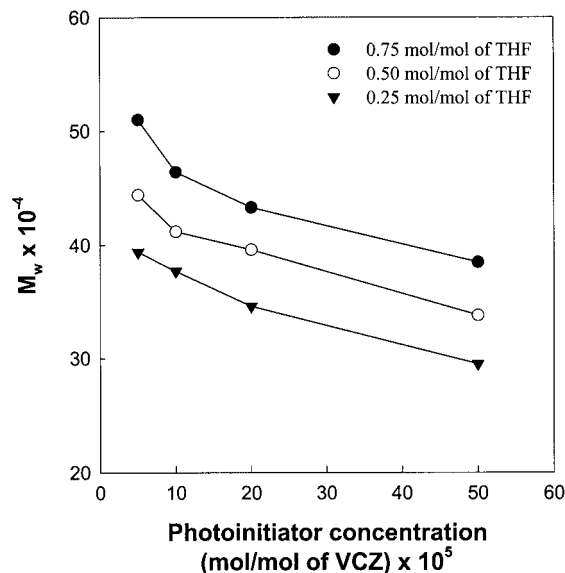


Figure 3 M_w of PVCZ polymerized in THF at -20°C with ADMVN concentration.

THF at -20°C using an ADMVN concentration of 0.00005 mol/mol of VCZ. It was deduced that the higher the VCZ concentration, the higher the conversion. At high monomer concentration, the radicals generated from the initiator preferably attack the double bonds of monomer molecules, which possess high electron density, conclusively, a higher rate of polymerization results. It has been known that, in the case of free radical solution polymerization of vinyl monomer at polymerization temperatures above 60°C using AIBN or BPO, it is very difficult to control the process if the monomer concentration is high because the latent heat accelerates the reaction. This indicates that autoacceleration may lead to excessive chain transfer during polymerization if the monomer concentration is high. However, Figure 2 presents that such acceleration revealing the sigmoidal-shaped curve seems not to be so noticeable during the low-temperature polymerization of VCZ in THF using photoinitiation even for highest monomer concentration of 0.75 mol/mol of THF. Therefore, it is obvious that low polymerization temperature is necessary in obtaining HMW PVCZ by free radical solution polymerization.

Molecular characteristics of PVCZ polymerized

In the radiation-initiated radical polymerization, the kinetic chain length, ν , is related to the concentration of photoinitiator by eq. (10)³⁸

$$\nu = (k_p/k_t^{0.5}) ([M]/I_0\phi I\epsilon [I])^{0.5} \quad (10)$$

This equation implies that the molecular weight of the polymer is increased with increasing monomer concentration and/or with decreasing initiator con-

centration. Figure 3 shows the effects of monomer and initiator concentration on M_w of PVCZ produced in THF at -20°C . PVCZ was sampled at similar conversions of about 30% to clarify the effects of monomer and initiator concentration. In accordance with the predictions by eq. (10), the M_w of PVCZ was increased as monomer concentration was increased or initiator concentration was decreased. Molecular weight of PVCZ was much higher at lower photoinitiator concentrations and at higher VCZ concentrations. PVCZ with the highest M_w of 510,000 was obtained when the polymerization was carried out at minimum photoinitiator concentration of 0.00005 mol/mol of VCZ. Below this photoinitiator concentration, effective polymerization could not occur. Figure 4 presents the effect of polymerization temperature on M_w of PVCZ produced in THF using a monomer concentration of 0.75 mol/mol of the solvent. PVCZ was sampled at similar conversion of about 30% to precisely clarify the polymerization temperature effect only. Molecular weight increased with a decrease in the polymerization temperature. These results indicate that higher polymerization temperature promotes transfer reactions and decreases molecular weight.

To identify the effects of polymerization temperature and conversion on the molecular weight distribution of the PVCZ polymerized, GPC experiments were performed obtaining the polydispersity index. Figure 5 shows results. From the fact that in the case of -20°C a lower polydispersity index of below 1.8 was obtained, it was concluded that low-temperature solution polymerization of VCZ in THF produced linear HMW PVCZ. The M_w and polydispersity index of PVCZ formed in THF at -20°C were 510,000 and 1.73, respectively.

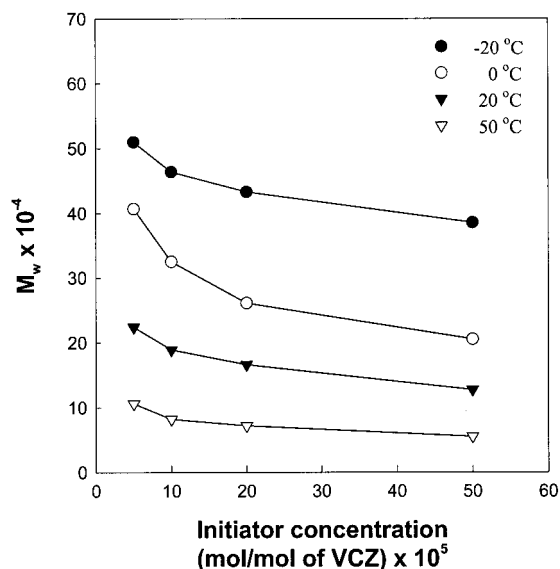


Figure 4 M_w of PVCZ polymerized in THF using a VCZ concentration of 0.75 mol/mol of THF with ADMVN concentration.

Optical transparency of PVCZ film is a very important factor for application to optical devices. Effects of polymerization temperature and conversion on degree of lightness were shown in Figure 6. Optical turbidity was increased with increasing polymerization temperature. At all polymerization temperatures, as the conversion increased by the procession of polymerization reaction, the clarity of PVCZ film was decreased, and this tendency was furthered at higher polymerization temperatures.

CONCLUSIONS

Considering the effect of various polymerization parameters on the conversion, molecular weight, its distribution, and whiteness of PVCZ, we could conclude as below: through a series of calculation using the initial-rate method, it was found that the photo-solution polymerization rate of VCZ in THF was proportional to the 0.47 powers of ADMVN concentration. As is well known, it is not easy to obtain linear HMW PVCZ by free radical polymerization at a polymerization temperature of over 50°C. However, UV-ray-initiated solution polymerization seemed to be advantageous in enhancing a molecular weight of PVCZ because it allowed the use of polymerization temperature down to -20°C. Conclusively, for PVCZ prepared in THF at -20°C using an ADMVN concentration of 0.00005 mol/mol of VCZ, a weight-average molecular weight of 510,000 was obtained, with a polydispersity index of 1.73, and a degree of lightness converged to about 99%. In the near future, we will report on the photo-initiated low-temperature heterogeneous solution polymerization of VCZ to increase both conversion and molecular weight.

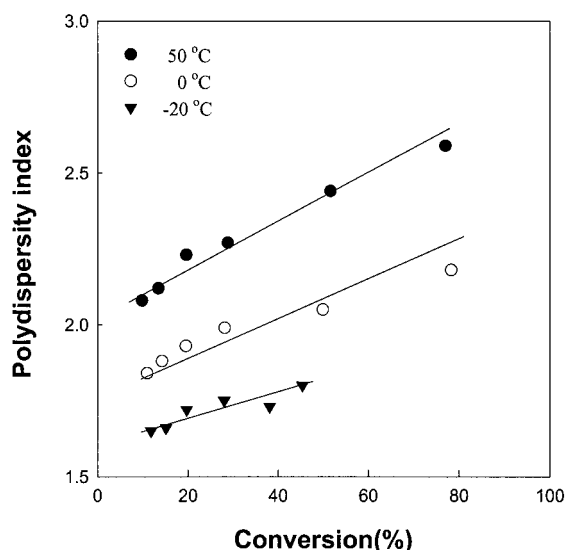


Figure 5 Polydispersity index of PVCZ prepared using a VCZ concentration of 0.75 mol/mol of THF and an ADMVN concentration of 0.00005 mol/mol of VCZ with conversion.

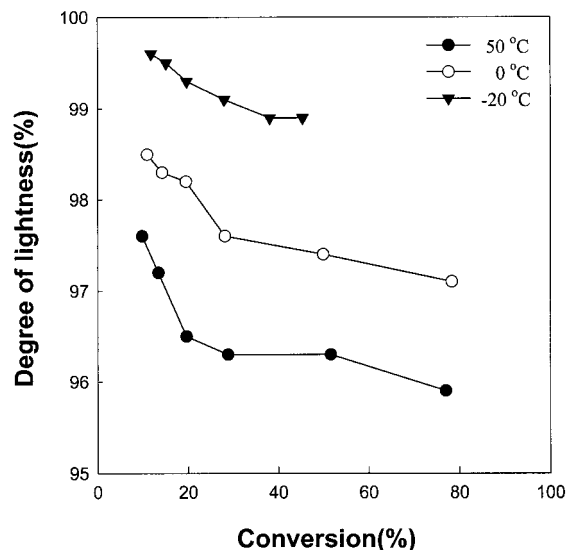


Figure 6 Degree of lightness of PVCZ prepared using a VCZ concentration of 0.75 mol/mol of THF and an ADMVN concentration of 0.00005 mol/mol of VCZ with conversion.

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