Room Temperature Polymerization of N-vinylcarbazole in Tetrahydrofuran

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Abstract: N-Vinylcarbazole (VCZ) was solution-polymerized in tetrahydrofuran (THF) at 25, 35, and 45 °C using a room temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN); the effects of amount of solvent, polymerization temperature, and initiator concentration were investigated. On the whole, the experimental results corresponded to predicted ones. Room polymerization temperature using ADMVN proved to be successful in obtaining poly(N-vinylcarbazole) (PVCZ) of high molecular weight with small temperature rise during polymerization, nevertheless of free radical polymerization by azoinitiator. The 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 25 °C using ADMVN concentration of 0.00005 mol/mol of VCZ, weight-average molecular weight of 221,000 was obtained, with polydispersity index of 2.05, and degree of lightness converged to about 99 %.

Keywords: VCZ, Solution-polymerized, THF, Room temperature, PVCZ

Introduction

Poly(N-vinylcarbazole) (PVCZ) has been a major subject of material science because it can be used as 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 form of uniform film, especially thick film above 100 μm thickness for photo-refractive application. To apply to these fields, it is essential to prepare PVCZ of high molecular weight and linearity by adopting new method to polymerize N-vinylcarbazole (VCZ) [14-16].

Until now, several methods have been developed for the polymerization of VCZ such as free radical [16-19], conventional cation (protonic acids, Lewis acids, carbocations) [20-24], photo-initiation [25,26], Ziegler-Natta [27], charge transfer [28], electrochemical [29,30], vapor deposition [15], and solid state [31]. Free radical polymerization of VCZ using azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) as initiators has been used to prepare PVCZ of molecular weight of below 100,000 [16,18,19]. In free radical bulk polymerization of VCZ, increased polymerization rate arising from greater temperature rises at higher polymerization temperature lowered 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. 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 make it unfavorable to obtain HMW PVCZ [16,18,19]. This is more problematic for conventional solution polymerization usually conducted at temperatures above 40 °C. Moreover, polymerization at temperature below 40 °C was only possible by the use of cation [20-24], photo-initiation [25,26], Ziegler-Natta [27], charge transfer [28], and electrochemical [29,30] methods. The above polymerization processes, however, inevitably require very complicate and expensive polymerization apparatus and special polymerization initiator and hence difficult to be commercialized.

In the preparation 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, a room temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN) [32-35], which can reduce the polymerization temperature down to room temperature, was selected for solution polymerization of VCZ in THF by simple free radical initiation to obtain HMW PVCZ. To evaluate the effects of polymerization conditions on the polymerization behavior of VCZ, the kinetic study of the free radical polymerization of VCZ in THF initiated by ADMVN has been performed.

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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 initiator ADMVN (Wako Co.) was recrystallized at low temperature twice from absolute methanol. Other extra-pure grade reagents were used without further purification.

Polymerization

VCZ was placed in a three-necked round bottom flask and flushed with dry nitrogen. The solvent, THF, was added into flask to dissolve the solid monomer and flushed with nitrogen for 3 h to eliminate oxygen. At the predetermined polymerization temperature, ADMVN was added to the solution. When polymerization had been completed, the product was precipitated by pouring into a large amount of methanol. The coagulated polymers were reprecipitated several times into methanol and then dried under vacuum at 50 °C for 24 h. Conversion was calculated by measuring the weight of the polymer. Conversions were averaged of five determinations. The detailed polymerization conditions are given in Table 1.

Characterization

Molecular weight of PVCZ was calculated by equation (1) [36]:

$$[\eta] = 1.44 \times 10^{-4} [M_w]^{0.65} \tag{1}$$

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

The molecular weight distribution and polydispersity index (M_w/M_n) were obtained by gel permeation chromatography (GPC). Water's GPC Model 515 equipped with a bank of four Styragel columns using THF as a solvent. The calculations were based on a calibration curve obtained with 12 polystyrene molecular weight standards with range of 2,500-2,000,000 $(M_w = 2,500, 4,000, 20,000, 35,000, 50,000, 90,000, 200,000, 400,000, 600,000, 900,000, 1,000,000, 2,000,000)$ purchased from Aldrich. The molecular weight of the sample is the polystyrene equivalent molecular weight. The lightness of

Table 1. Parameters for solution polymerization of VCZ

Type of initiator	ADMVN
Type of solvent	THF
Initiator concentration	0.00005 mol/mol of VCZ
	0.0001 mol/mol of VCZ
	0.0005 mol/mol of VCZ
Monomer concentration	0.25 mol/mol of THF
	0.50 mol/mol of THF
	1.00 mol/mol of THF
Temperature	25, 35, 45 °C

the PVCZ film was measured by Color eye (I. D. I., model C).

Results and Discussion

The rate of polymerization (R_p) may be expressed classically by equation (2) [37] for a free radical polymerization:

$$R_p = k_p \left(\frac{fk_d}{k_t}\right)^{0.5} [M][I]^{0.5} \tag{2}$$

where f is the initiator efficiency, $[M]$ and $[I]$ are the concentrations of monomer and initiator, and k_d, k_p, and k_t are reaction rate constants of initiator decomposition, propagation, and termination, respectively. This expression implies that the rate of polymerization is determined by the efficiency and concentration of initiator. Figure 1 presents the initial conversion rate in the solution polymerization of VCZ in THF at 25 °C using three different ADMVN concentrations. It was shown that the greater the initiator concentration, the higher the polymerization rate, in agreement with equation (2).

The dependence of polymerization rate on initiator concentration can be determined by a kinetic study called initial-rate method [38]. Polymerization rate can be expressed by the exponential forms of reaction reagents. In early stage of polymerization, reaction rate is coincided with the slope of conversion-time relation. For small changes in initial concentration of one reagent with the other hold constant, the ratio of 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 equations (3)-(9):
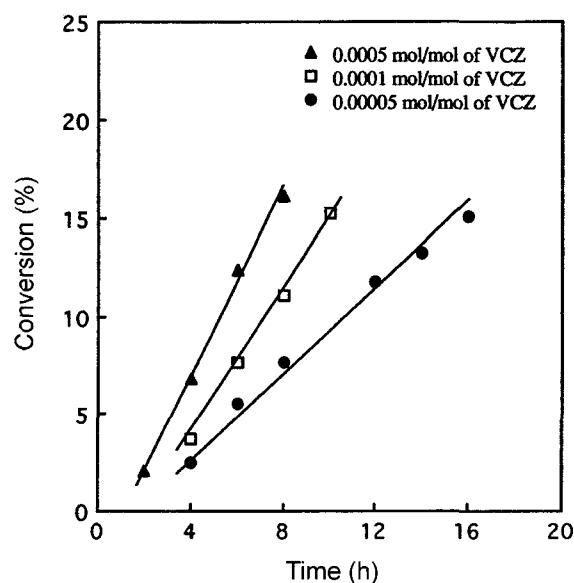
Figure 1. Conversion of VCZ into PVCZ in early stage of polymerization in THF at 25 °C using VCZ concentration of 1 mol/mol of THF.

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

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

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

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

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

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

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

This procedure can be used to determine all exponents like n_1, n_2, and n_3. In this study, $[I]_1$, $[I]_2$, and $[I]_3$ were used as 0.0005, 0.0001, and 0.00005, respectively, and $(R_p)_1$, $(R_p)_2$, and $(R_p)_3$ were, respectively, obtained from the three slopes in Figure 1. From the calculation, it was found that the polymerization rate of VCZ in THF was proportional to the 0.47 powers of ADMVN concentration. That is in good accordance with theoretical prediction by equation (2).

Figure 2 shows the effect of monomer concentration on the conversion of VCZ into PVCZ polymerized in THF at 25 °C using ADMVN at 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 temperature of 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 sigmoidal shaped curve seems not to be so noticeable during the room temperature polymerization of VCZ in THF using ADMVN even for monomer concentration of 1 mol/mol of THF. Therefore, it is obvious that low polymerization temperature is necessary in obtaining HMW PVCZ by free radical solution polymerization.

Effect of initiator concentration on the conversion of VCZ into PVCZ prepared in THF at 25 °C using monomer concentration of 1 mol/mol of solvent is shown in Figure 3. The conversion rate was increased as the ADMVN concentration was increased. This result well agreed to the previous data described in Figure 1.

Figure 4 presents conversion-time plots for temperatures of 25, 35, and 45 °C at monomer concentration of 1 mol/mol of solvent and initiator concentration of 0.00005 mol/mol of VCZ. The rate of conversion was increased with increasing polymerization temperature. At the higher polymerization temperatures of 45 and 35 °C, the conversion-time curves had the characteristic sigmoidal shape showing the increase in rate of polymerization with conversion. That is, the rate of conversion was relatively higher in the early stage of polymerization at 45 and 35 °C but the ultimate conversion rate was lower in both cases. In contrast, at 25 °C, the conversion linearly increased without any abrupt changes in the slope. This might be
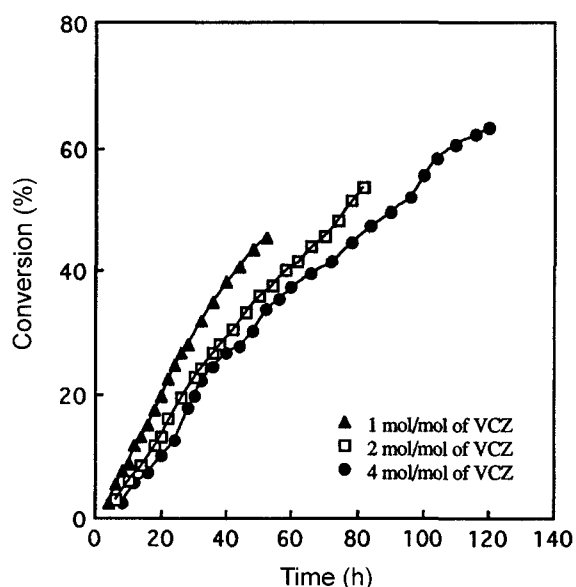

Figure 2. Conversion of VCZ into PVCZ polymerized in THF at 25 °C using ADMVN concentration of 0.00005 mol/mol of VCZ with polymerization time.
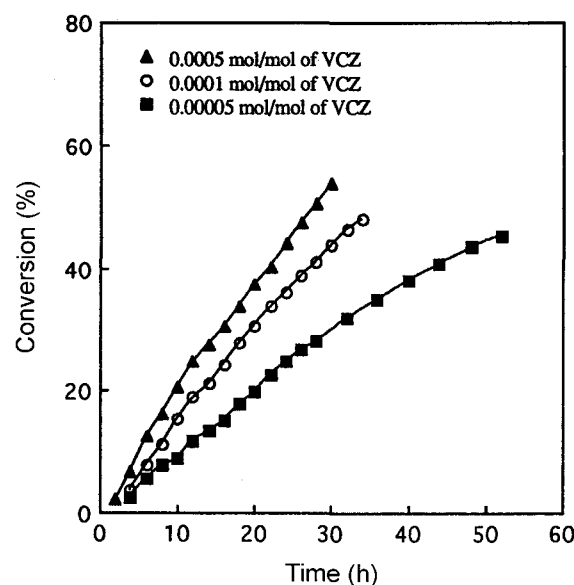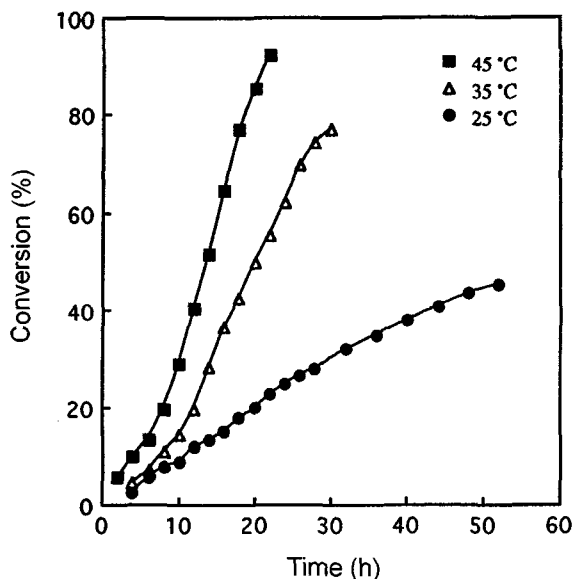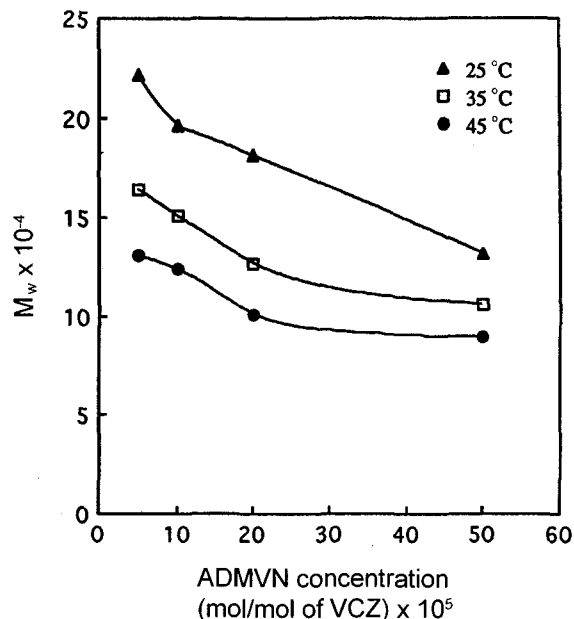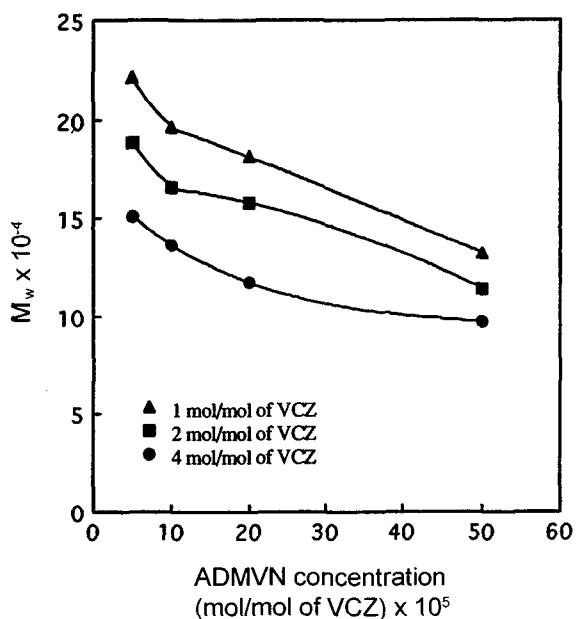

Figure 3. Conversion of VCZ into PVCZ polymerized in THF at 25 °C using VCZ concentration of 1 mol/mol of THF with polymerization time.

Figure 4. Conversion of VCZ into PVCZ polymerized in THF using VCZ concentration of 1 mol/mol of THF and ADMVN concentration of 0.00005 mol/mol of VCZ with polymerization time.

Figure 5. M_w of PVCZ polymerized in THF at 25 °C with ADMVN concentration.

explained by smaller heating effects during polymerization at lower polymerization temperature using ADMVN.

In radical polymerization, the kinetic chain length, v, is related to f and $[I]$ by equation (10) [36]:

$$v = k_p [M]/2(f k_d k_t [I])^{0.5} \quad (10)$$

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

Figure 6. M_w of PVCZ polymerized in THF using VCZ concentration of 1 mol/mol of THF with ADMVN concentration.

with decreasing initiator concentration. Figure 5 shows effects of monomer and initiator concentration on M_w of PVCZ produced in THF at 25 °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 equation (10), 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 ADMVN concentrations and at higher VCZ concentrations. Figure 6 presents the effect of polymerization temperature on M_w of PVCZ produced in THF using monomer concentration of 1 mol/mol of solvent. PVCZ was sampled at similar conversion of about 30 %. 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 7 shows results. From the fact that in the case of 25 °C, a lower value of polydispersity index (ca. 1.8-2.0) was obtained, it was concluded that low temperature solution polymerization of VCZ in THF produced linear HMW PVCZ. M_w and polydispersity index of PVCZ formed in THF at 25 °C were 221,000 and 2.05, respectively.

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 8. Optical turbidity was increased with increasing polymerization temperature. At all polymerization temperatures, as the conversion increased by the procession
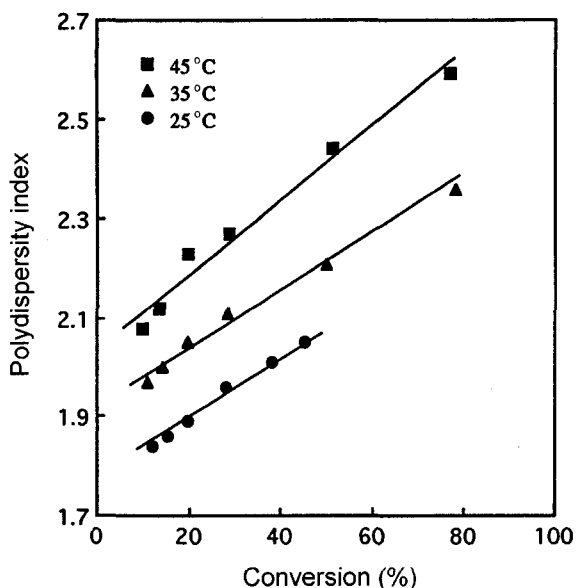
Figure 7. Effect of polymerization temperature and conversion on the polydispersity index of PVCZ prepared using VCZ concentration of 1 mol/mol of THF and ADMVN concentration of 0.00005 mol/mol of VCZ.
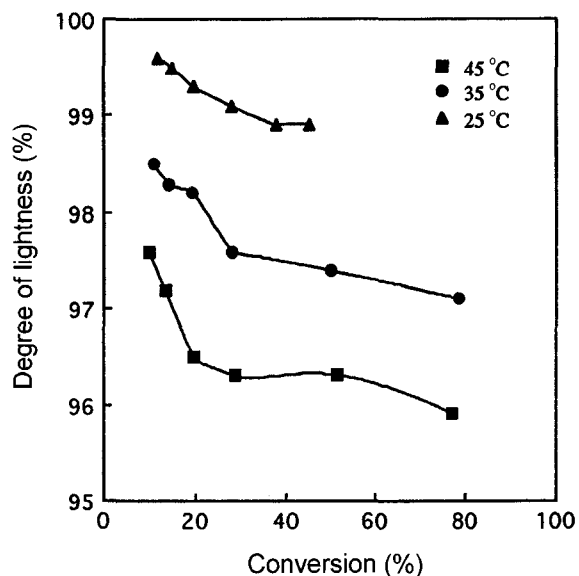
Figure 8. Degree of lightness of PVCZ prepared using VCZ concentration of 1 mol/mol of THF and ADMVN concentration of 0.00005 mol/mol of VCZ.

of polymerization reaction, the clarity of PVCZ film was decreased and this tendency was furthered at higher polymerization temperatures.

Conclusions

As well known, it is not easy to obtain linear HMW PVCZ

by free radical polymerization initiated with AIBN or BPO. However, a room temperature initiator, ADMVN, seemed to be advantageous in lowering polymerization rate of VCZ because it allowed the use of polymerization temperature down to *ca.* 25 °C. Hence, ADMVN was more effective in preparing HMW PVCZ by simple free radical polymerization without using special initiation methods and complex polymerization apparatus such as high vacuum or irradiation. In the near future, we will report on the low temperature polymerization of VCZ using low chain transfer solvent.

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