

Solution Polymerization Behavior of N-Vinylcarbazole by Low-Temperature Azoinitiator

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ABSTRACT: N-Vinylcarbazole (VCZ) was solution polymerized in 1,1,2,2-tetrachloroethane (TCE) at 30, 40, and 50°C using a low-temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN); the effects of polymerization temperature and concentrations of initiator and solvent were investigated. On the whole, the experimental results corresponded to predicted ones. Low-polymerization temperature using ADMVN proved to be successful in obtaining poly(N-vinylcarbazole) (PVCZ) of high molecular weight with smaller temperature rise during polymerization, nevertheless of free radical polymerization by azoinitiator. The polymerization rate of VCZ in TCE was proportional to the 0.46 power of ADMVN concentration. The molecular weight was higher and the molecular weight distribution was narrower with PVCZ polymerized at lower temperatures. For PVCZ produced in TCE at 30°C using ADMVN concentration of 0.00005 mol/mol of VCZ, weight-average molecular weight of 271 000 was obtained, with polydispersity index of 1.66. © 2000 John Wiley & Sons, Inc. *J Appl Polym Sci* 76: 1558–1563, 2000

Key Words: VCZ; low temperature; ADMVN; PVCZ; high molecular weight

INTRODUCTION

Poly(N-vinylcarbazole) (PVCZ) is a promising polymer for good photo-conductors,^{1–3} charge-transfer complexes,³ electroluminescent devices,⁴ and photo-refractive materials.^{5–9} To prepare uniform film (especially thick film above 100 μm thickness for photo-refractive application) having good performance for various applications described above, it is required to increase molecular weight and linearity of

PVCZ by adopting new methods to polymerize N-vinylcarbazole (VCZ).^{10–12}

In general, several methods have been developed for the polymerization of VCZ, e.g., free radical,^{12,13} conventional cation (protonic acids, Lewis acids, carbocations),^{14–16} photo-initiation,¹⁷ Ziegler-Natta,¹⁸ charge transfer,¹⁹ electrochemical,²⁰ vapor deposition,¹¹ and solid state,²¹ and so on. It is well known that low-molecular-weight PVCZ with number-average molecular weight of below 100 000 is prepared by free radical polymerization of VCZ using azobisisobutyronitrile (AIBN) or benzoyl peroxide (BPO)^{12,13} as an initiator. In free radical bulk polymerization of

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VCZ, increased polymerization rate arising from greater temperature rises at higher polymerization temperature lowered molecular weight of PVCZ. Thus high-molecular-weight (HMW) PVCZ is hardly obtained. To reduce the self-heating of the medium, free radical solution polymerization of VCZ was tried. This solution polymerization method has advantages of easy control of polymerization exotherm and of higher conversion than those of bulk polymerization. These polymerizations, however, were conducted at temperatures above 40°C. Moreover, polymerization at temperatures below 40°C was only possible by the use of cation,^{14–16} photo-initiation,¹⁷ Ziegler-Natta,¹⁸ charge transfer,¹⁹ and electrochemical²⁰ methods. The above polymerization processes, however, inevitably require very complicate and expensive polymerization apparatus and special polymerization initiator and hence difficult to be commercialized.

For preparation methods of high-performance PVCZ film by solution casting, the molecular parameters of PVCZ such as molecular weight, molecular weight 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 structure of PVCZ.

In this study, a low-temperature initiator, 2,2'-azobis(2,4-dimethylvaleronitrile) (ADMVN),^{22,23} which can reduce the polymerization temperature down to room temperature, was selected for solution polymerization of VCZ by simple free radical initiation to obtain HMW PVCZ. 1,1,2,2-Tetrachloroethane (TCE) with low chain-transfer constant was used as a solvent. To identify the effects of polymerization conditions on the polymerization behavior of VCZ, the kinetics of the free radical polymerization of VCZ in TCE initiated by ADMVN has been examined.

EXPERIMENTAL

Materials

VCZ (Aldrich Co.) was purified by recrystallization from n-hexane, 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.

Table I Parameters for Solution Polymerization of VCZ

Type of initiator	ADMVN
Type of solvent	TCE
Initiator concentration	0.00005 mol/mol of VCZ 0.0001 mol/mol of VCZ 0.0005 mol/mol of VCZ
Monomer concentration	0.4 mol/mol of TCE 0.2 mol/mol of TCE 0.1 mol/mol of TCE
Temperature	30°C, 40°C, 50°C

Polymerization

VCZ was placed in a three-necked round bottom flask and flushed with dry nitrogen. The TCE 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 averages of five determinations. The detailed polymerization conditions are given in Table I.

Characterization

Molecular weight of PVCZ was calculated by eq. (1)²⁴:

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

(in tetrahydrofuran [THF] at 25°C)

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). Waters' GPC Model 515 equipped with a bank of four Styragel columns using THF as a solvent.

RESULTS AND DISCUSSION

In a free radical polymerization, the rate of polymerization (R_p) may be expressed by eq. (2)²⁵:

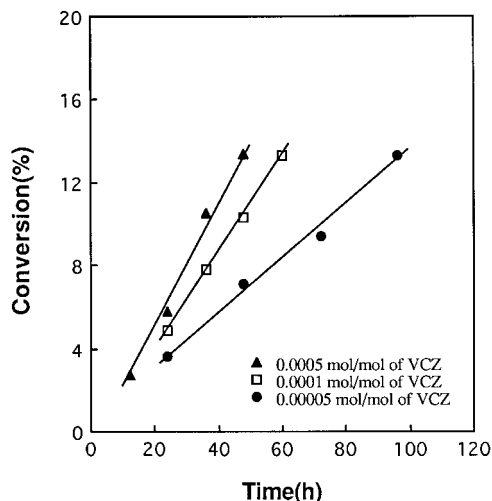


Figure 1 Conversion of VCZ into PVCZ in early stage of polymerization in TCE at 30°C using VCZ concentration of 0.4 mol/mol of solvent.

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

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 predicts that the rate of polymerization is increased as the efficiency and concentration of initiator are increased. Figure 1 presents the initial conversion rate measured within 15% conversion in the solution polymerization of VCZ in TCE at 30°C using three different ADMVN concentrations. 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 initiator concentration can be determined by the initial-rate method.²⁶ For small changes in initiator concentration, the polymerization rate can be approximated to the corresponding ratio of increments. If a measurement is made at two different initiator concentrations of one component with the other held constant, the order with respect to that component can be simply determined by using eqs. (3) through (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 such as n_1 , n_2 , n_3 . From the calculation, it was found that the polymerization rates of VCZ in TCE was proportional to the 0.46 power of ADMVN concentrations. That is, in some accord with eq. (2), the polymerization rate in TCE was proportional to $[ADMVN]^{0.46}$.

Figure 2 shows the effect of monomer concentration on the conversion of VCZ into PVCZ polymerized in TCE at 30°C using ADMVN at 0.00005 mol/mol of VCZ. It was shown that the higher the VCZ concentration, the higher the conversion. At higher monomer concentration, the radicals generated from the initiator largely 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 excessive polymerization exotherm accelerates the polymerization. This indicates that autoacceleration may lead to exces-

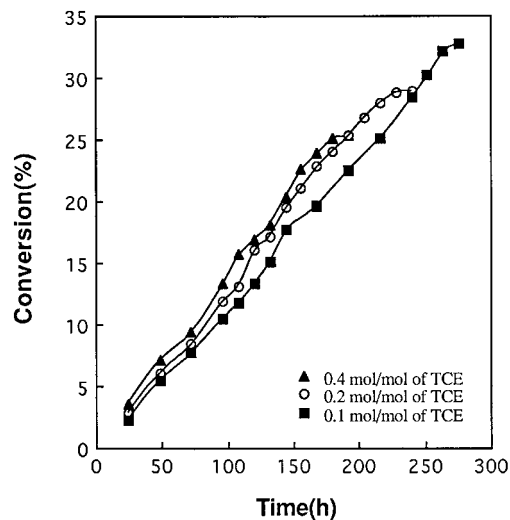


Figure 2 Conversion of VCZ into PVCZ polymerized in TCE at 30°C using ADMVN concentration of 0.00005 mol/mol of VCZ with polymerization time.

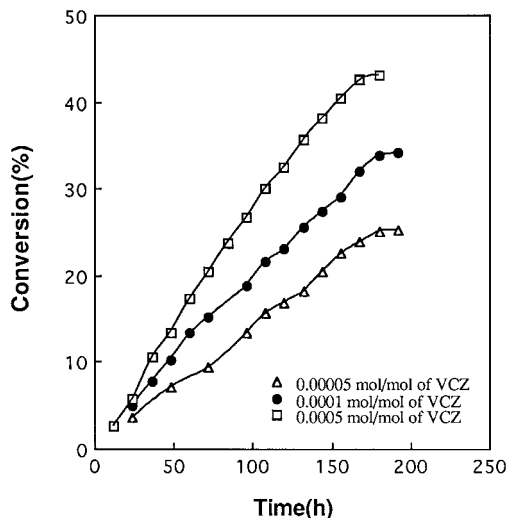


Figure 3 Conversion of VCZ into PVCZ polymerized in TCE at 30°C using VCZ concentration of 0.4 mol/mol of solvent with polymerization time.

sive chain transfer during polymerization if the monomer concentration is high. However, Figure 2 presented that such autoacceleration revealing sigmoidal shaped curve seems not to be so noticeable during the low-temperature polymerization of VCZ in TCE using ADMVN even for a concentration of monomers of 0.4 mol/mol of TCE. Conclusively, 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 produced in TCE at 30°C using monomer concentration of 0.4 mol/mol of solvent are presented 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 30, 40, and 50°C at monomer concentration of 0.4 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 50 and 40°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 50 and 40°C but the ultimate conversion rate was lower in both cases. In contrast, at 30°C, the conversion linearly increased without any abrupt changes in

the slope. This might be explained by smaller heating effects during polymerization at lower polymerization temperature using ADMVN.

In radical polymerization, the kinetic chain length, ν , is related to f , and $[I]$ by equation (10)²⁵:

$$\nu = k_p[M]/2(fk_dk_i[I])^{0.5} \quad (10)$$

This equation predicts that the molecular weight of polymer is increased with increasing monomer concentration and/or with decreasing initiator concentration. Figure 5 shows effects of monomer and initiator concentrations on M_w of PVCZ produced in TCE at 30°C. PVCZ was sampled at similar conversions of about 20% to clarify the effects of monomer and initiator concentrations. In accordance with the predictions by eq. (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 TCE using monomer concentration of 0.4 mol/mol of solvent. PVCZ was sampled at similar conversion of about 20%. Molecular weight increased with a decrease in the polymerization temperature. These results indicate that higher polymerization temperature pro-

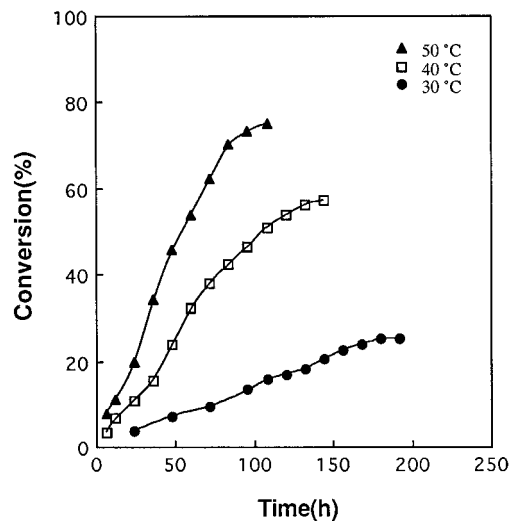


Figure 4 Conversion of VCZ into PVCZ polymerized in TCE using VCZ concentration of 0.4 mol/mol of solvent and ADMVN concentration of 0.00005 mol/mol of VCZ with polymerization time.

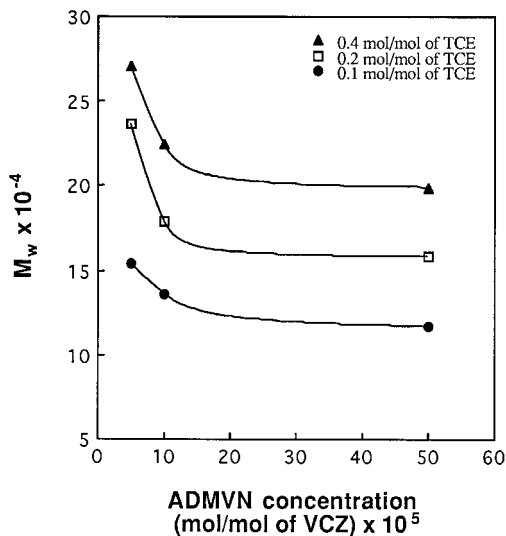


Figure 5 M_w of PVCZ polymerized in TCE at 30°C with ADMVN concentration.

notes transfer reactions and decreases molecular weight.

In this study, to identify the effects of polymerization temperature and conversion on the molecular weight distribution of the PVCZ polymerized, the polydispersity index was obtained through GPC experiments. Figure 7 shows results. From the fact that in the case of 30°C, a lower value of ca. 1.6–1.7 was obtained, it was concluded that low-temperature solution polymerization of VCZ in TCE produced linear HMW

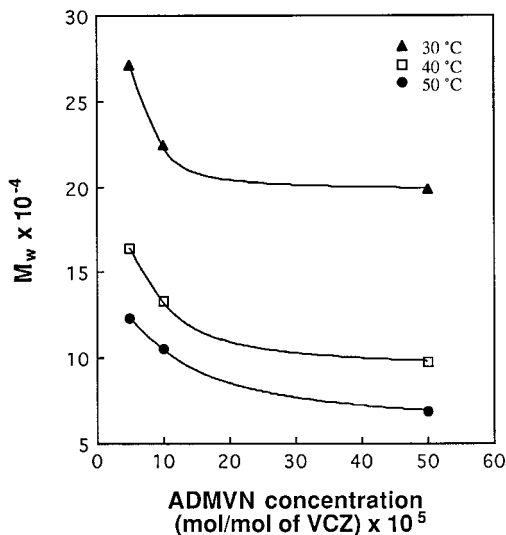


Figure 6 M_w of PVCZ polymerized in TCE using VCZ concentration of 0.4 mol/mol of solvent with ADMVN concentration.

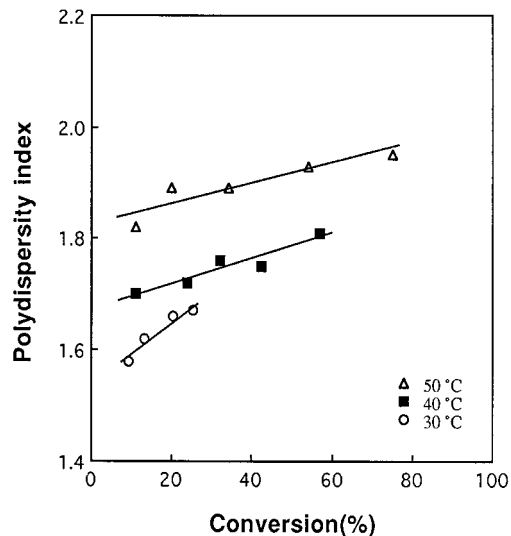


Figure 7 Effect of polymerization temperature and conversion on the polydispersity index of PVCZ prepared using VCZ concentration of 0.4 mol/mol of solvent and ADMVN concentration of 0.00005 mol/mol of VCZ.

PVCZ. M_w and polydispersity index of PVCZ formed in TCE at 30°C were 271 000 and 1.66, respectively.

CONCLUSION

As is well known, it is not an easy job to obtain linear HMW PVCZ by free radical polymerization initiated with AIBN or BPO. However, a lower temperature initiator, ADMVN, seemed to be advantageous in lowering polymerization rate of VCZ because it allowed the use of polymerization temperature down to ca. 30°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 irradiation method. In the near future, we will report on the heterogeneous-solution polymerization of VCZ to increase both conversion and molecular weight.

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