Preparation of High-Molecular-Weight Poly(*N*-vinylcarbazole) by the Photoinduced Low-Temperature Solution Polymerization of *N*-Vinylcarbazole in 1,1,2,2-Tetrachloroethane

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ABSTRACT: For the preparation of high-molecular-weight (HMW) poly(*N*-vinylcarbazole) (PVCZ) with a narrow molecular weight distribution, *N*-vinylcarbazole (VCZ) was solution-polymerized in 1,1,2,2-tetrachloroethane (TCE) at −20, 0, and 20°C with photoinitiation. The effects of the polymerization temperature and the concentrations of the polymerization solvent and photoinitiator on the polymerization behavior and molecular parameters of PVCZ were investigated. A low polymerization temperature with photoirradiation was successful in obtaining HMW PVCZ with a smaller temperature rise during polymerization than that for thermal free-radical polymerization by azobisisobutyronitrile (AIBN). The photo-solution-polymerization rate of VCZ in TCE was proportional to $[AIBN]^{0.45}$. The molecular weight was higher and the molecular weight distribution was narrower for PVCZ made at lower temperatures. For PVCZ prepared in TCE at −20°C with a photoinitiator concentration of 0.00003 mol/mol of VCZ, a weight-average molecular weight of 920,000 was obtained, with a polydispersity index of 1.46, and the degree of transparency converged to about 99%. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2391–2396, 2003

INTRODUCTION

Poly(*N*-vinylcarbazole) (PVCZ) is a promising material for photoconductors,[1,2] charge-transfer complexes,[1–3] electroluminescent devices,[4–6] and photorefractive materials.[7–10] For the preparation of uniform films, especially films greater than 100 μm thick, for photorefractive applications with the good performance needed for the aforementioned applications, it is essential for the molecular weight and linearity of PVCZ to be increased by the adoption of a new method of polymerizing *N*-vinylcarbazole (VCZ).[11–13]

Several methods have been developed for the polymerization of VCZ, such as free-radical,[13–16] conventional cationic (protonic acids, Lewis acids, and carbocations),[17–21] photoinitiation,[22,23] Ziegler–Natta,[24] charge-transfer,[25] electrochemical,[26,27] vapor-deposition,[12] and solid-state polymerization.[28] The free-radical polymerization of VCZ with azobisisobutyronitrile (AIBN) and benzoyl peroxide (BPO) as thermal initiators gives PVCZ with a molecular weight below 100,000.[16,18,19] In the free-radical bulk polymerization of VCZ, an increased polymerization rate (R_p) arising from greater temperature increases at higher polymerization temperatures causes a lowering of the molecular weight of PVCZ. High-molecular-weight (HMW) PVCZ cannot be obtained by this method. For a reduction in the heat effect and the viscosity of the reaction medium, the free-radical polymerization of VCZ is conducted in solution. Solution polymerization has the advantage of easy control over the viscosity at higher conversions. However, frequent chain transfer to the monomer makes it unfavorable for obtaining HMW PVCZ of a superior molecular structure.[13,15,16] This is more difficult for conventional solution polymerization, which is usually conducted at temperatures greater than 40°C.

In this study, we used low-temperature photoirradiation polymerization,[29] which is superior to chemical initiation in producing linear HMW PVCZ because of the relatively lower propagation rate of polymerization and the lower probability of termination. Therefore, to increase the molecular weight and linearity and to minimize side reactions, we polymerized VCZ by ultraviolet (UV) irradiation in solution at −20,
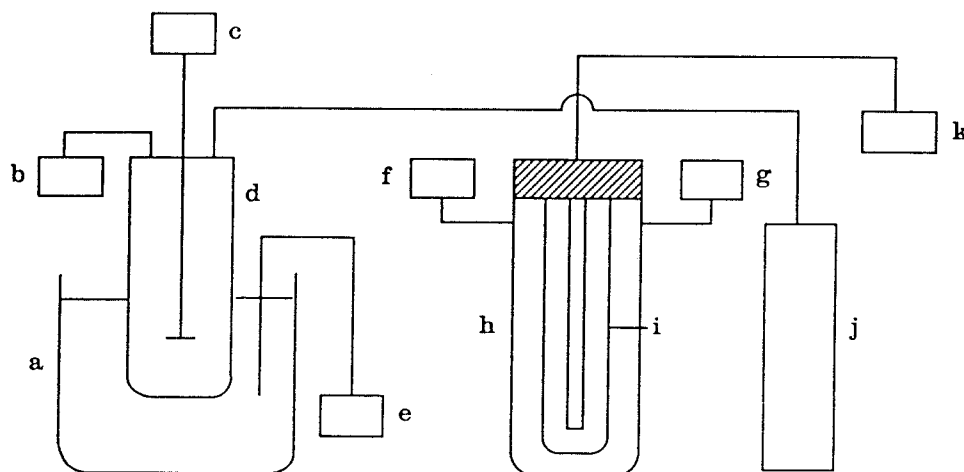
Figure 1 Apparatus used for the photopolymerization of VCZ: (a) low-temperature bath, (b) nitrogen outlet, (c) mechanical stirrer, (d) polymerization reactor, (e) temperature sensor, (f) coolant inlet, (g) coolant outlet, (h) lamp cooling tube, (i) high-pressure mercury lamp, (j) nitrogen bomb, and (k) 500-W power supply.

0, and 20°C. 1,1,2,2-tetrachloroethane (TCE) with a low chain-transfer constant was used as a solvent. To identify the effects of the polymerization conditions on the polymerization behavior of VCZ, we undertook a kinetic study of the polymerization of VCZ in TCE initiated by UV. In addition, the effects of the proportion of the solvent, the polymerization temperature, and the photoinitiator concentration on the conversion of VCZ into PVCZ and the molecular weight, molecular weight distribution, and transparency of the resulting PVCZ were investigated.

EXPERIMENTAL

Materials

VCZ (Aldrich Co., Milwaukee, WI) was purified by recrystallization from *n*-hexane and dried *in vacuo* at 30°C for 2 days (melting point = 65.5°C). The photoinitiator AIBN (Wako Co., Osaka, Japan) was recrystallized at a low temperature twice from absolute methanol. Other extra-pure-grade reagents were used without further purification.

Polymerization

Our polymerization apparatus is shown in Figure 1. VCZ and TCE were added in a Pyrex tube, which was placed in a low-temperature methanol bath and flushed with N_2 for 4 h. After the polymerization temperature was established and AIBN had been added, the mixture was irradiated with a high-pressure 500-W Hg lamp. For comparison with UV initiation results, the thermal solution polymerization of VCZ was conducted at 50°C. When the polymerization was complete, the polymer was purified by reprecipitation from tetrahydrofuran (THF)/methanol.

After the removal of the monomer from the polymer *in vacuo* was complete, the conversion was calculated gravimetrically. The quoted conversions were the averages of three determinations. The polymerization conditions are listed in Table I.

Characterization

The molecular weight of PVCZ was calculated as follows:[30]

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

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

The molecular weight distribution and polydispersity index (weight-average molecular weight/number-average molecular weight) were obtained by gel permeation chromatography (GPC). A Waters GPC model 515 (MA) was used that was equipped with a bank of four Styragel columns with THF as a solvent.

TABLE I
Photo-Solution-Polymerization Conditions of VCZ

Type of photoinitiator	AIBN
Type of solvent	TCE
Photoinitiator concentration	0.00003 mol/mol of VCZ
	0.00005 mol/mol of VCZ
	0.0001 mol/mol of VCZ
	0.0002 mol/mol of VCZ
Monomer concentration	0.2 mol/mol of TCE
	0.4 mol/mol of TCE
	0.6 mol/mol of TCE
Temperature	−20, 0, and 20°C
Radiation type	UV
Radiation source	High-pressure mercury lamp (500 W)

The calculations were based on a calibration curve obtained with 14 polystyrene molecular weight standards over the 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, and 8,500,000) purchased from Aldrich. The molecular weights of the samples were the polystyrene equivalent molecular weights.

Homogeneous 1.0 g/dL solutions of PVCZs in TCE obtained at polymerization temperatures of −20, 0, and 50°C were poured onto stainless steel trays and dried at room temperature to produce films. The transparency of the PVCZ film was measured with a Color Eye instrument (model C, IDI, NY).

RESULTS AND DISCUSSION

In general, radiation-initiated bulk polymerization might be used for the production of HMW polymers 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 minimized. The initiation rate can be changed easily. Therefore, R_p and the molecular weight can be controlled. General photoinitiators used for the radical polymerization of vinyl monomers are azo, benzoin, and benzophenone types. Azo and benzoin types are cleavage-type photoinitiators. However, benzophenone is a hydrogen-abstraction type; its initiation rate is slower and its initiation mechanism is more complex than those of cleavage-type photoinitiators.[31] In this study, to identify the effect of a photoinitiator on the molecular weight and conversion of the resultant polymer, we used the azo compound AIBN (R—N=N—R), which is decomposed into free radicals by UV.

In the radiation-initiated radical polymerization, R_p may be expressed as follows:[32]

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

where I_0 is the incident light intensity; ϕ is the quantum yield; l is the path length; ϵ is the extinction coefficient of the photoinitiator; [I] and [M] are the concentrations of the photoinitiator and monomer, respectively; and k_p and k_t are the reaction rate constants of propagation and termination, respectively. This expression implies that R_p rises with an increasing concentration of the photoinitiator. Figure 2 shows the effect of the initiator concentration on the conversion of VCZ into PVCZ prepared in TCE at −20°C with a monomer concentration of 0.6 mol/mol of solvent.

The dependence of R_p on the initiator concentration can be determined with the initial-rate method.[33,34] For small changes in the initiator concentration, R_p can be approximated to the corresponding ratio of the
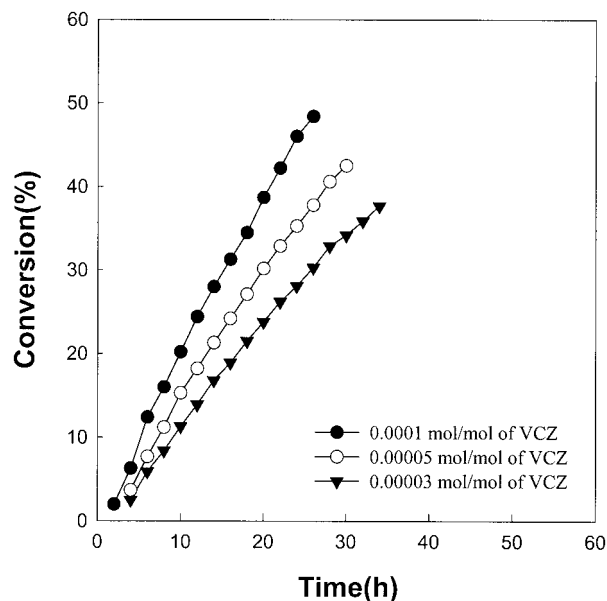
Figure 2 Conversion of VCZ into PVCZ polymerized in TCE at −20°C with a VCZ concentration of 0.6 mol/mol of TCE with the polymerization time.

initiator concentrations. 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 determined as follows:

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

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

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

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

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

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

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

This procedure can be used to determine all exponents such as n_1, n_2, and n_3. Therefore, in this study, from calculations with the kinetic parameters obtained from plots of conversion (up to 15%) with the polymerization time in Table II, we found that the photopolymerization rate of VCZ in TCE at −20°C was proportional to [AIBN]^{0.45}, in good agreement with the theoretical prediction by eq. (2).

Th effect of the monomer concentration on the conversion of VCZ into PVCZ polymerized in TCE at −20°C with AIBN at 0.00003 mol/mol of VCZ is presented in Figure 3. It was deduced that the higher the

TABLE II
Kinetic Parameters Used for the Calculation of the Initiator Exponent at a Polymerization Temperature of $-20°C$

$(R_p)_1$ (% h^{-1})	2.41
$(R_p)_2$ (% h^{-1})	1.89
$(R_p)_3$ (% h^{-1})	1.41
$[I]_1$ (mol/mol of VPi)	0.0001
$[I]_2$ (mol/mol of VPi)	0.00005
$[I]_3$ (mol/mol of VPi)	0.00003
$(R_p)_1/(R_p)_2$	1.26
$(R_p)_2/(R_p)_3$	1.34
$(R_p)_3/(R_p)_1$	0.59
$[I]_1/[I]_2$	2.00
$[I]_2/[I]_3$	1.67
$[I]_3/[I]_1$	0.30
n_{2a}	0.33
n_{2b}	0.57
n_{2c}	0.44
n_2	0.45

VCZ concentration was, the higher the conversion was. At high monomer concentrations, the radicals generated from the initiator preferably attacked the double bonds of monomer molecules, which possessed high electron density, and a higher R_p value resulted. It is known that, for the free-radical solution polymerization of vinyl monomers at temperatures above 60°C with AIBN or BPO, it is very difficult to control the process if the monomer concentration is high because the heat of reaction causes self-heating. This indicates that autoacceleration may lead to excessive chain transfer during polymerization if the monomer concentration is high. However, Figure 3 shows that such acceleration, revealed by a sigmoidal curve,
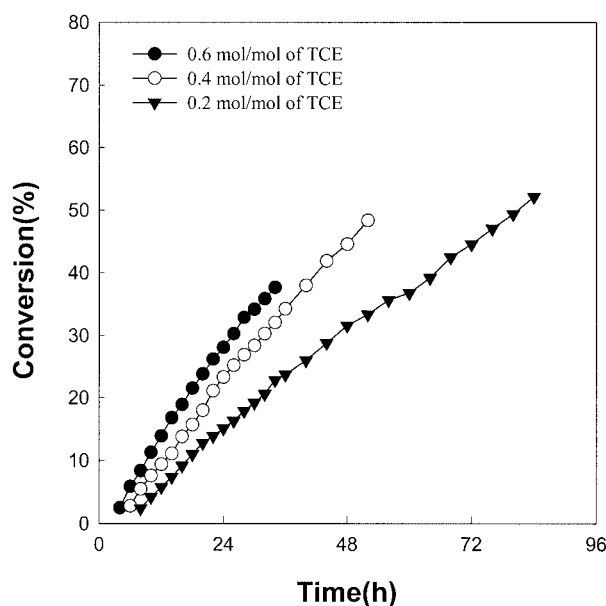

Figure 3 Conversion of VCZ into PVCZ polymerized in TCE at $-20°C$ with an AIBN concentration of 0.00003 mol/mol of VCZ with the polymerization time.
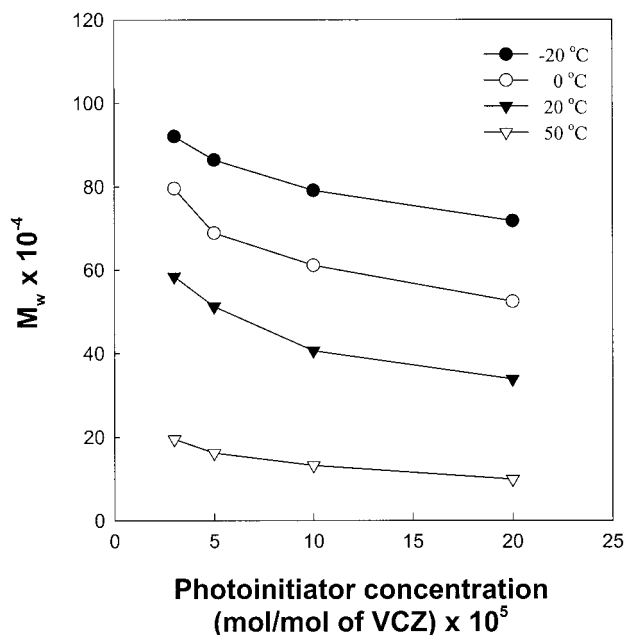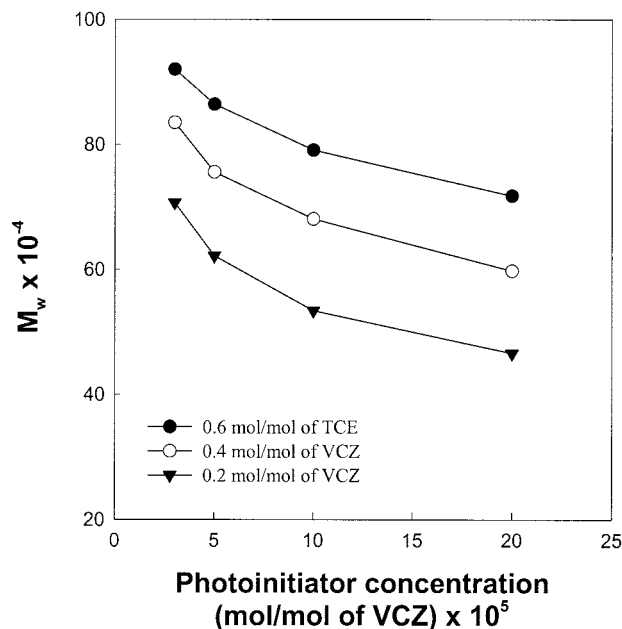

Figure 4 M_w of PVCZ polymerized in TCE with a VCZ concentration of 0.6 mol/mol of TCE with the AIBN concentration.

was not so noticeable during the low-temperature polymerization of VCZ in TCE with photoirradiation, even for a monomer concentration of 0.6 mol/mol of TCE. Therefore, it is obvious that a low polymerization temperature is necessary to obtain HMW PVCZ by free-radical solution polymerization.

In the radiation-initiated radical polymerization, the kinetic chain length (ν) is related to the concentration of the photoinitiator:[32]

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

This equation implies that the molecular weight of the polymer is increased with an increasing monomer concentration and/or with a decreasing initiator concentration. Figure 4 shows the effect of the polymerization temperature on M_w of PVCZ produced in TCE with a monomer concentration of 0.6 mol/mol of solvent. PVCZ was sampled at a similar conversion of about 30%. The molecular weight increased with a decrease in the polymerization temperature. These results indicated that a higher polymerization temperature favored transfer reactions and reduced the molecular weight. Figure 5 shows the effects of the monomer and initiator concentrations on M_w of PVCZ produced in TCE at $-20°C$. We sampled PVCZ at similar conversions of about 30% to clarify the effects of the monomer and initiator concentrations. In agreement with the predictions of eq. (10), M_w of PVCZ increased as the monomer concentration was increased or the initiator concentration was decreased. The molecular weight of PVCZ was much higher at

Figure 5 M_w of PVCZ polymerized in TCE at −20°C with the AIBN concentration.

lower AIBN concentrations and at higher VCZ concentrations. PVCZ with the highest M_w of 920,000 was obtained when the polymerization was carried out at the maximum monomer concentration in the solvent (0.6 mol/mol of TCE) and at the minimum photoinitiator concentration of 0.00003 mol/mol of VCZ. Below this photoinitiator concentration, effective polymerization did not occur.

To identify the effects of the polymerization temperature and conversion on the molecular weight distribution of PVCZ, we performed GPC experiments to obtain the polydispersity index. Figure 6 shows the results. Because at −20°C a value below 1.5 for the polydispersity index was obtained, we concluded that the low-temperature solution polymerization of VCZ in TCE produced linear HMW PVCZ. For PVCZ with a conversion of about 30%, formed in TCE at −20°C, the values of M_w and the polydispersity index were 920,000 and 1.46, respectively.

The optical transparency of PVCZ film is a very important factor for applications in optical devices. Figure 7 shows the effects of the polymerization temperature and conversion on the degree of transparency. The optical turbidity was increased with an increasing polymerization temperature. At all polymerization temperatures, as the conversion increased during polymerization, the clarity of the PVCZ film decreased, and this tendency was more prominent at higher polymerization temperatures.

CONCLUSIONS

It is known that it is very difficult to obtain linear HMW PVCZ by free-radical polymerization initiated
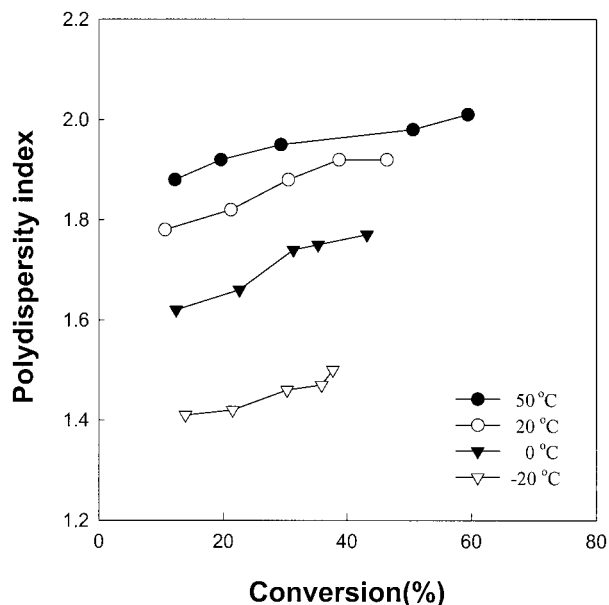
Figure 6 Polydispersity index of PVCZ prepared with a VCZ concentration of 0.6 mol/mol of TCE and an AIBN concentration of 0.00003 mol/mol of VCZ with the conversion.

with AIBN or BPO at polymerization temperatures greater than 50°C. However, the UV-initiated solution polymerization of VCZ in TCE seemed to be advantageous in enhancing the molecular weight and linearity of PVCZ because it allowed the use of polymerization temperatures as low as −20°C. For PVCZ prepared in TCE at −20°C with an AIBN concentration of 0.00003 mol/mol of VCZ and a VCZ concentration of
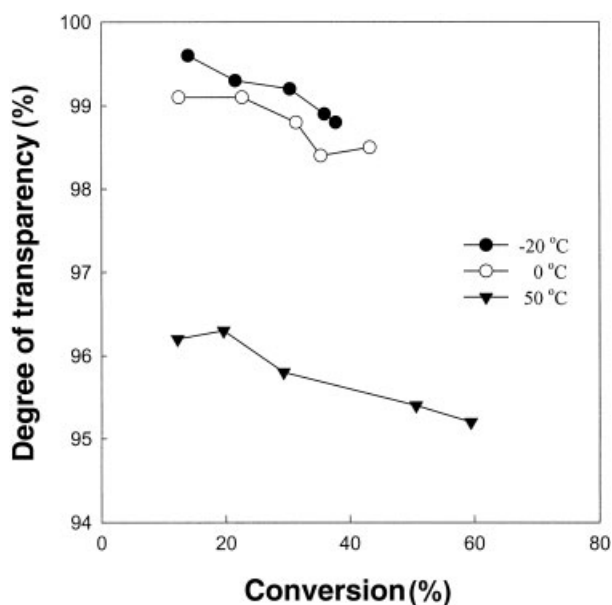
Figure 7 Degree of transparency of PVCZ prepared with a VCZ concentration of 0.6 mol/mol of TCE and an AIBN concentration of 0.00003 mol/mol of VCZ with the conversion.

0.6 mol/mol of TCE, an M_w value of 920,000 was obtained, with a polydispersity index of 1.46, and the degree of transparency converged to about 99%. In the near future, we will report on the photoinitiated low-temperature precipitation polymerization of VCZ used to increase both the conversion and molecular weight.

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