

Living Cationic Polymerization of *N*-Vinylcarbazole with Iodine

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ABSTRACT: Living cationic polymerization of *N*-vinylcarbazole (NVC) has successfully been achieved with iodine initiator in both polar (CH_2Cl_2) and less polar ($\text{CH}_2\text{Cl}_2\text{-CCl}_4$, 1/1, v/v) solvents at -50°C . Under these conditions, the molecular weight of polymers increased linearly with increasing conversion, and it further increased on addition of a new-monomer feed to a completely polymerized solution. The number-average molecular weights of the polymers produced in a $\text{CH}_2\text{Cl}_2\text{-CCl}_4$ (1/1, v/v) mixture were in fair agreement with theoretical values based on the assumption that one initiator molecule yields one polymer chain. At a higher temperature (-15°C), living poly(NVC) could be obtained only in a nonpolar solvent (toluene). Polymerizations by oxo acids (CF_3COOH , $\text{CH}_3\text{SO}_3\text{H}$, and $\text{CH}_3\text{COCIO}_4$) or BF_3OEt_2 failed to give living polymers even at low temperatures. It was concluded that long-lived propagating species are generated specifically by iodine initiator from a monomer giving a stable carbocation with an electron-donating substituent.

KEY WORDS *N*-Vinylcarbazole / *p*-Methoxystyrene / Iodine / Oxo Acids / Metal Halides / Cationic Polymerization / Living Polymer / Molecular Weight Distribution / Propagating Species /

It has been difficult to obtain living polymers in the cationic polymerization of vinyl compounds because of the low stability of propagating carbocations that promote transfer and/or termination reactions. We have speculated that living cationic polymers can be formed when a moderately stable propagating cation carries a nucleophilic counteranion in its close vicinity (nondissociated state) so that it may be protected from undesirable side-reactions. This requires that a monomer with an electron-donating group be polymerized in a non-polar solvent with an initiator giving a nucleophilic counteranion. This idea has been justified recently by the formation of living polymers from *p*-methoxystyrene (*p*-MOS) with iodine initiator at low temperatures.^{1,2}

The present work examines the applicability of our principle for living polymers to the polymerization of NVC which produces a stable propagating

carbocation as *p*-MOS.

Hereafter, as in the previous paper,² the term "living" means a long lifetime of the propagating species that may possibly undergo transfer or termination reactions to a small extent.

Two previous studies are relevant to the living cationic polymerization of NVC. Rooney³ reported that the degree of polymerization of the poly(NVC) prepared with a stable cationic salt approached the ratio of monomer to initiator concentrations at low temperature where transfer reactions should be suppressed. However, no further investigation was done from the standpoint of living polymerization. Stannett *et al.*⁴ obtained block copolymers of NVC and vinyl ethers with a stable cationic salt, but the polymerization of NVC under their conditions, though terminationless, suffered from frequent transfer. Thus no well-defined living polymerization of NVC has yet been attained.

Diagnostic criteria for living polymerization are (1) the linear increase of the molecular weight of polymers with increasing conversion and (2) its

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further increase on addition of a new-monomer feed at the end of the first polymerization. In this study, the living nature of NVC polymerizations by a variety of initiators was investigated in terms of these criteria. We wish to report that the iodine-initiated polymerization of NVC gives living polymers under selected conditions.

EXPERIMENTAL

Materials

NVC (Nakarai Chemicals) was purified by recrystallizing three times from hexane and stored in the dark. Commercial iodine and trifluoroacetic acid (CF_3COOH) (guaranteed reagents) were used without further purification. Boron trifluoride etherate (BF_3OEt_2) and methanesulfonic acid ($\text{CH}_3\text{SO}_3\text{H}$) were distilled under reduced pressure. Acetyl perchlorate (AcClO_4) was synthesized as described elsewhere.⁵ Toluene, carbon tetrachloride (CCl_4), and methylene chloride (CH_2Cl_2) as solvents were washed successively with concentrated sulfuric acid, water, aqueous 10% NaOH solution, and water, and were then distilled over CaH_2 just before use.

Procedures

The polymerization of NVC was conducted under dry nitrogen by injecting an initiator solution into a monomer solution (0.20 M). The polymerization system contained 0.2–0.3 mM of water as impurity. After a certain interval, methanol containing a small amount of aqueous ammonia was added to terminate the reaction. The products were precipitated in a large amount of methanol, filtered off, and then dried *in vacuo*. Conversion was determined from the weight of recovered polymers.

The molecular-weight distribution (MWD) of the polymers was measured in tetrahydrofuran by gel-permeation chromatography (GPC) on a Toyo Soda Model-HLC 801A chromatograph equipped with two columns packed with GMH6 polystyrene gel. The GPC curves were calibrated against standard polystyrene. The polydispersity (M_w/M_n) was evaluated from MWD curves.

RESULTS AND DISCUSSION

Polymerization with Iodine

The polymerization of NVC by iodine was

performed at 0, -15 , and -50°C in solvents of different polarities.

Polymerization at 0°C . Figure 1 shows the time-conversion curve for the polymerization at 0°C in a nonpolar solvent, toluene, and the MWD of the product polymers. The first polymerization was completed within 40 min in which the polymer molecular weight increased with increasing conversion. At the end of the first reaction, a new-monomer feed was added to the solution. The second-stage polymerization indeed ensued, but it was so slow as to need *ca.* 24 h to reach 100% conversion. This rate reduction perhaps resulted from the inactivation of the propagating species by

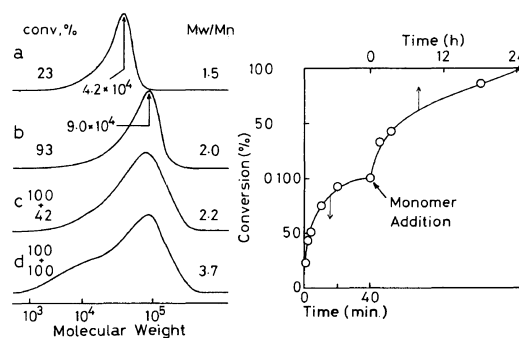


Figure 1. Time-conversion curve for the polymerization of NVC by iodine at 0°C in toluene and the MWD of product polymers before (a, b) and after (c, d) monomer addition: $[\text{I}_2]_0 = 0.3 \text{ mM}$; $[\text{M}]_0 = 0.20 \text{ M}$; $[\text{M}]$ (on monomer addition) = 0.20 M .

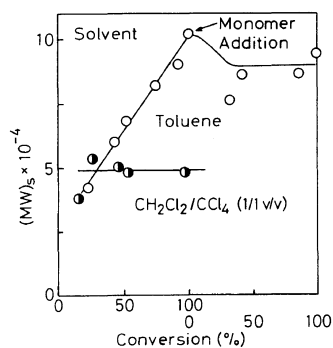


Figure 2. Relationship between conversion and the peak molecular weight (MW_s) of the MWD curve for poly(NVC) obtained with iodine at 0°C in two solvents: $[\text{M}]_0 = 0.20 \text{ M}$; $[\text{M}]$ (on monomer addition) = 0.20 M . $[\text{I}_2]_0$: \circ , 0.30 mM ; \bullet , 0.12 mM .

product polymers having basic nitrogen atoms. The MWD curves in Figure 1 indicate that the polymer molecular weight failed to increase on monomer addition.

Figure 2 illustrates the effect of solvent polarity on the relationship between conversion and the molecular weight of polymers. $(MW)_s$ represents the peak molecular weight of a MWD curve based on a polystyrene calibration. The polymer molecular weight was independent of conversion in the relatively polar solvent ($\text{CH}_2\text{Cl}_2\text{-CCl}_4$).

Thus, at 0°C living polymers could not be obtained with iodine initiator.

Polymerization at -15°C . Figure 3 shows the MWD of the polymers produced at -15°C in two solvents before and after monomer addition. In both solvents, the second-monomer feed polymerized to high conversion but more slowly than the first. In toluene, the MWD curve shifted to higher molecular weight with increasing conversion. The molecular weight further increased with conversion after addition of a new-monomer feed. The molecular weight $(MW)_s$ vs. conversion plot for toluene (Figure 4) was linear before and after the monomer addition.

On the other hand, in $\text{CH}_2\text{Cl}_2\text{-CCl}_4$ (1/1, v/v), a more polar solvent, $(MW)_s$ increased with increasing conversion only during the first polymerization and it leveled off after the monomer addition. The MWD of polymers broadened significantly with the progress of polymerization as indicated by the large

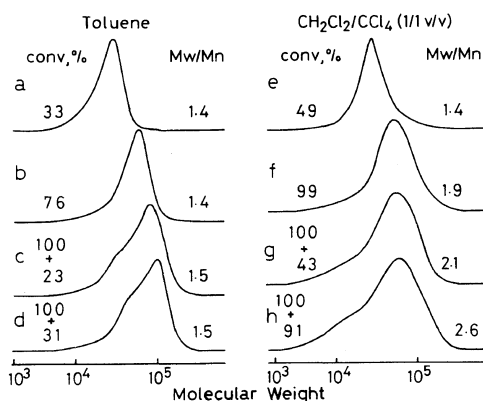


Figure 3. MWD of poly(NVC) produced by iodine at -15°C before (a, b; e, f) and after (c, d; g, h) monomer addition: solvents as indicated; $[\text{I}_2]_0 = 0.50 \text{ mM}$; $[\text{M}]_0 = 0.20 \text{ M}$; $[\text{M}]$ (on monomer addition) = 0.20 M .

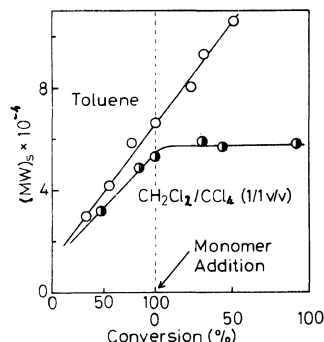


Figure 4. Relationship between conversion and the peak molecular weight $(MW)_s$ of the MWD curve for poly(NVC) obtained with iodine at -15°C in two solvents. Polymerization conditions are the same as in Figure 3.

M_w/M_n ratios given in Figure 3. The reason for these phenomena is not clear, but they suggest that transfer reactions to polymer take place in the second-stage polymerization in which a large amount of polymer is already present.

The results described above show that at -15°C , long-lived propagating species can be formed in a nonpolar solvent such as toluene but cannot be in a more polar medium. Even in toluene, however, the MWD of the polymers produced after the monomer addition had a tailing in the lower molecular-weight region and a large M_w/M_n ratio. This suggests that transfer reactions took place following the monomer addition to some extent at -15°C .

Polymerization at -50°C . At -50°C , CH_2Cl_2 and its mixture with CCl_4 (1/1, v/v) were used as solvents, since NVC is insoluble in toluene. In both solvents, as at the higher temperatures, the first polymerization was quantitative and a new-monomer feed, added to the completely polymerized solution, was consumed to high conversion, although the second-stage reaction was much slower than the first.

Figure 5 shows the MWD of the polymers obtained before and after the monomer addition at -50°C . Regardless of the solvent polarity, the MWD curves shifted toward higher molecular weights with conversion without tailing and they shifted further after the monomer addition. It should be emphasized that the MWD at -50°C was very narrow, independent of conversion, with M_w/M_n ratios of 1.2–1.4.

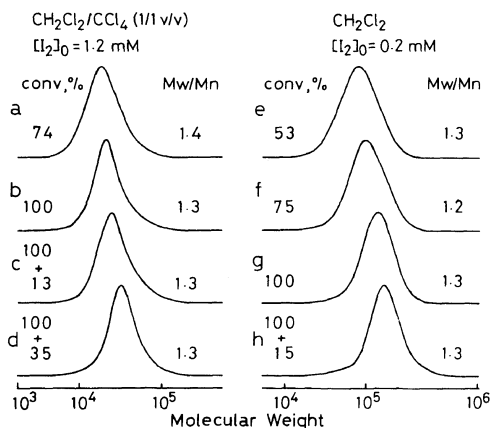


Figure 5. MWD of poly(NVC) produced with iodine at -50°C before (a, b; e, f) and after (c, d; g, h) monomer addition: solvents as indicated; $[\text{M}]_0 = 0.20 \text{ M}$; $[\text{M}]$ (on monomer addition) = 0.20 M .

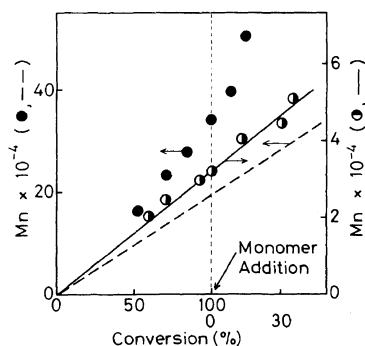


Figure 6. M_n vs. conversion plots for poly(NVC) obtained with iodine at -50°C : circles, observed; lines, calculated (see text). Solvent and $[\text{I}_2]_0$: (●, —), CH₂Cl₂-CCl₄ (1/1, v/v), 1.2 mM; (●, ----), CH₂Cl₂, 0.20 mM. $[\text{M}]_0 = 0.20 \text{ M}$, $[\text{M}]$ (on monomer addition) = 0.20 M .

Figure 6 compares the calculated and observed number-average molecular weights (M_n) of polymers produced in two solvents at -50°C . The observed M_n was obtained viscometrically under the theta condition (in toluene at 37°C) on the basis of a $[\eta]-M_n$ relationship⁶ for poly(NVC) having M_w/M_n values similar to those in this work. The theoretical M_n was calculated under the assumption that one initiator molecule produces one polymer chain. The solid and dashed lines in Figure 6 show its dependence on conversion for CH₂Cl₂-CCl₄ and

CH₂Cl₂, respectively. The observed M_n increased almost linearly with increasing conversion in either CH₂Cl₂-CCl₄ or CH₂Cl₂ solvent before and after the monomer addition. In CH₂Cl₂-CCl₄, furthermore, the calculated values are in fair agreement with the observed values. This shows the almost perfect "living" nature of the polymerization in CH₂Cl₂-CCl₄ (1/1, v/v) at -50°C . The disagreement between the experimental (closed circle) and the theoretical (dashed line) values in polar CH₂Cl₂ solvent can be ascribed to the consumption of a part of the initiator by adventitious impurities or certain side-reactions.

Under similar conditions, polymerization with iodine was conducted to high conversion in the presence of a dead poly(NVC) that was obtained with iodine initiator at -50°C . Recovery of the dead polymer confirmed the absence of an increase in its molecular weight to exclude any possible grafting of the propagating species onto the dead poly(NVC), which would also have increased the polymer molecular weight.

The low temperature (-50°C) has thus allowed the living polymerization of NVC in both polar and nonpolar solvents. This is in sharp contrast to the formation of living polymers only in a nonpolar solvent at -15°C .

Polymerization with Other Initiators

Possibilities of living NVC polymerization were

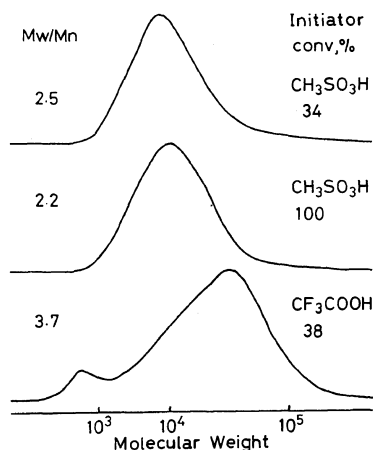


Figure 7. MWD of poly(NVC) obtained with oxo acids at -50°C in a CH₂Cl₂-CCl₄ (1/1, v/v) mixture: $[\text{M}]_0 = 0.20 \text{ M}$; $[\text{M}]$ (on monomer addition) = 0.20 M . $[\text{Initiator}]_0$: CH₃SO₃H, 0.42 mM; CF₃COOH, 15 mM.

Table I. Conditions for living cationic polymerizations of *N*-vinylcarbazole (NVC) and *p*-methoxystyrene (*p*-MOS) with iodine^a

Monomer	Nonpolar solvent		Polar solvent		
	0°C	-15°C	0°C	-15°C	-50°C
<i>p</i> -MOS	○	○	×	×	—
NVC	△	○	×	△	○

^a ○, The polymer molecular weight increased linearly with increasing conversion before and after monomer addition; △, The polymer molecular weight increased linearly with conversion only during the first polymerization and leveled off after monomer addition; ×, The polymer molecular weight was independent of conversion.

also examined with various initiators other than iodine in a CH₂Cl₂-CCl₄ (1/1, v/v) mixed solvent at -50°C. Figure 7 gives the results with oxo acids (CH₃SO₃H and CF₃COOH) that are less active and hence will yield counteranions of strong nucleophilicity.

The polymerization by CH₃SO₃H (0.42 mM) was completed within 4 h, and a monomer feed added at this stage polymerized smoothly. However, the molecular weight of the polymers remained constant independent of conversion and their MWD (Figure 7) was much broader ($M_w/M_n=2.5$) than that of the living polymer obtained with iodine.

The polymerization with CF₃COOH (15 mM) stopped before its completion, indicating the involvement of a termination reaction. In addition, the MWD of the polymer obtained at the limiting conversion was broad (Figure 7). Therefore, the oxo acids failed to produce living polymers even at low temperature.

Some experiments were also carried out with strong initiators, CH₃COCIO₄ and BF₃OEt₂, which give counterions of weak nucleophilicity. In CH₂Cl₂-CCl₄ (1/1, v/v) at -50°C these initiators completely polymerized NVC (0.20 M) in a very short time even at very low concentrations (0.010 mM for CH₃COCIO₄, 0.05 mM for BF₃OEt₂). The product polymers were insoluble in common organic solvents presumably because of cross-linking, and thus, their molecular weights could not be determined. No further attempt was made to analyze the polymerizations by the two initiators.

Comparison with Living *p*-MOS Polymerization

This study has clearly demonstrated that cationic

living polymers can be obtained not only from *p*-MOS^{2,3} but from NVC with iodine initiator under suitable conditions. Table I compares the conditions for living cationic polymerizations of these two monomers by iodine. The polymerization of NVC, in analogy with *p*-MOS, gave living polymers in less polar solvents at lower temperatures where transfer reactions are depressed.

On the other hand, at least at a low temperature (-50°C) the polymerization of NVC was still "living" even in a polar solvent in which living polymers could not be obtained from *p*-MOS. This means that a nondissociated propagating species is no longer essential to the living polymerization of NVC that forms a more stable carbocation than *p*-MOS.

In both NVC and *p*-MOS polymerizations, living polymers were produced specifically by iodine and could not be formed at all with other initiators such as metal halides and oxo acids. The counteranion derived from iodine, in spite of its strong nucleophilicity, may be much less active at low temperature in β-hydrogen elimination (transfer) than those from oxo acids.

In conclusion, the present work has shown that long-lived propagating species can be formed by iodine initiator in conjunction with a vinyl monomer giving a stable carbocation.

REFERENCES

1. T. Higashimura and O. Kishiro, *Polym. J.*, **9**, 87 (1977).
2. T. Higashimura, M. Mitsuhashi, and M. Sawamoto, *Macromolecules*, **12**, 178 (1979).
3. J. M. Rooney, *Makromol. Chem.*, **179**, 165 (1978).

4. J. M. Rooney, D. R. Squire, and V. T. Stannett, *J. Polym. Sci., Polym. Chem. Ed.*, **14**, 1877 (1976).
5. T. Masuda and T. Higashimura, *J. Macromol. Sci.*, *Chem.*, **A 5**, 547 (1971).
6. N. Kuwahara, S. Higashida, M. Nakata, and M. Kaneko, *J. Polym. Sci., A-2*, **7**, 285 (1969).