Ring Structure of Cyclic Poly(2-vinylpyridine) Proved by Pyrolysis−GC/MS

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Received December 14, 1998; Revised Manuscript Received August 2, 1999

ABSTRACT: Poly(2-vinylpyridine) (P2VP) with cyclic structure was tentatively prepared through the reaction of linear P2VP having two living ends followed by coupling with a bifunctional coupling agent. Thus, prepared crude product was fractionated by preparative size exclusion chromatography in order to enrich the cyclic polymer portion. Then the existence of the ring structure in the fractionated P2VP sample was directly confirmed for the first time by pyrolysis−gas chromatography/mass spectrometry by detecting the characteristic fragments reflecting the coupling moiety of the polymers at which the coupling agent combined the living 2VP units at both functional points.

Introduction

Ring polymers having no chain end are expected to have quite different natures from those of the corresponding linear ones. Therefore, the study of physical properties of ring polymers has been of interest for many years. Ring polymers are usually prepared by the reaction of the living polymers having functional groups on both ends with bifunctional linking agents. By this method, several cyclic polystyrenes[1−5] and poly(2-vinylpyridine)s[6,7] have been synthesized. In these studies, characterization of their ring structures was attempted by size exclusion chromatography (SEC),[1,2,5−7] viscosity measurement,[2−4,7] ultracentrifugation sedimentation,[5] and glass transition temperature (T_g) measurement.[6,7] The facts that the observed values for the polymer samples such as retention time in SEC resulting from the hydrodynamic volume, intrinsic viscosity, sedimentation constant, and T_g were meaningfully different from those of the corresponding linear ones should be regarded as indirect evidence of the existence of the ring polymers. So far, however, the ring structures of the cyclic polymers have not been directly proved through the characterization of chemical structures yet.

Recently, the authors developed a new highly sensitive method to determine trace amounts of terminal groups in various poly(methyl methacrylate)s by pyrolysis−gas chromatography/mass spectrometry (Py-GC/MS).[8,9] In this work, the ring structure of cyclic poly(2-vinylpyridine) (P2VP) was confirmed by the Py-GC/MS method. The P2VP sample containing ring structure was tentatively prepared by the reaction of linear P2VP having two living ends with α,α′-dibromo-*p*-xylene as a bifunctional coupling agent.[10] Thus, prepared crude product was then fractionated in order to enrich the cyclic polymer portion by removing multiply coupled products. The existence of the ring structure in the fractionated P2VP sample was confirmed by detecting the characteristic fragments reflecting the coupling moiety of the polymers in which the coupling agent combined with the living 2VP units in both functional points by using Py-GC/MS.

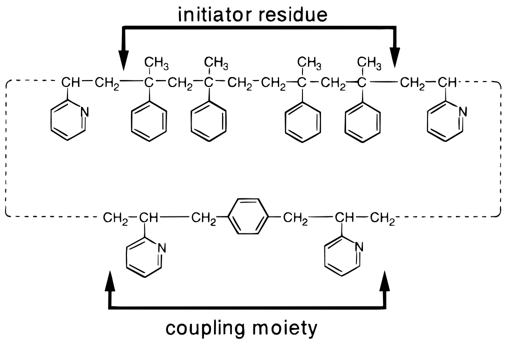

Figure 1. Possible structure of cyclic poly(2-vinylpyridine) [P2VP].

Experimental Section

Materials. 2VP monomer and tetrahydrofuran (THF), which is a solvent for both polymerization and coupling reactions, were highly purified before use.[11] The dipotassium salts of α-methylstyrene tetramer and *n*-butyllithium (*n*-BuLi) were prepared in the same manner as performed previously.[12] α,α′-Dibromo-*p*-xylene (Tokyo Kasei Kogyo Co., Ltd.) was recrystallized from solution in chloroform using *n*-hexane. The purified crystal was dissolved in THF, and the solution was evacuated and stored in an ampule. α-Bromo-*p*-xylene (Wako Pure Chemical Ind., Ltd.) was dried over calcium hydride under dry argon and distilled in vacuo.

Preparation of Cyclic Poly(2-vinylpyridine). A P2VP with two living ends was prepared by anionic polymerization of 2VP (ca. 2.1 g) using dipotassium salt of α-methylstyrene tetramer (1.10×10^{-4} mol) as an initiator under high vacuum (3×10^{-5} Torr) at −78 °C in THF (ca. 250 mL), and a part of solution including ca. 0.2 g of polymer was isolated to take out linear P2VP as a precursor. Then, its cyclization was carried out by reacting the living P2VP with 67% molar amount to the initiator (7.4×10^{-5} mol) of α,α′-dibromo-*p*-xylene in THF followed by terminating the excess living P2VP molecules with methanol. Figure 1 shows the possible molecular structure of the cyclic P2VP thus prepared. Here, a relatively low polymer concentration (ca. 0.8 g/dL) was adopted to lower the probability of the formation of multiply coupled products formed from plural precursor molecules.

Preparation of Linear Poly(2-vinylpyridine) Model Polymers. Three kinds of linear P2VP model polymers were prepared in order to use for identification of the characteristic fragments which reflect the coupling moiety in the cyclic P2VP

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10.1021/ma981921l CCC: $18.00

from the other many degradation products in Py-GC/MS. The model polymer named L-1 was synthesized by initiating with the dipotassium salt of α-methylstyrene tetramer followed by terminating with methanol. L-2 was prepared by initiating with *n*-BuLi followed by coupling with α,α′-dibromo-*p*-xylene and then terminating with methanol. L-3 was prepared by initiating with *n*-BuLi followed by terminating with α-bromo-*p*-xylene.

Size Exclusion Chromatography. The molecular weight distributions of the polymer samples were measured by using a size exclusion chromatograph (Tosoh model-HLC802A) equipped with two serially connected mixed-bed columns [Tosoh GMH$_{XL}$ (7.8 mm i.d. × 30 cm long) packed with 5 μm diameter of poly(styrene-*co*-divinylbenzene)gel having various pore sizes with an exclusion limit of 4×10^8]. THF containing 5% *N,N,N′,N′*-tetramethylethylenediamine (TMEDA) was used as the developing solvent at a flow rate of 1.0 mL/min. P2VP standards with narrow molecular weight distributions prepared by anionic polymerization were also used for calibration.

Fractionation. The crude product of the cyclization reaction was considered to be a mixture of linear molecules, cyclic molecules, and multiply coupled products. The multiply coupled products with more than twice the molecular weight of the others were able to be easily removed as a separated first peak by a preparative SEC using THF containing 5% TMEDA as the elution solvent at a flow rate of 5.0 mL/min for a SEC column [Tosoh G5000H6 (21.5 mm i.d. × 30 cm long) packed with 15 μm diameter of poly(styrene-*co*-divinylbenzene)gel with an exclusion limit 4×10^6]. Then the latter part (about 25%) of the second peak was fractionally collected in order to obtain a ring polymer-enriched fraction since, in general, SEC should yield slightly longer retention times for a given ring polymer than that of the corresponding linear one with the same molecular weight. By this procedure, ca.15% of the crude products was collected as the fractionated P2VP sample, R-1. The linear model P2VP coupled by α,α′-dibromo-*p*-xylene (L-2) was also purified by using preparative SEC to remove uncoupled fraction. The resulting number-average molecular weight (M_n) for R-1 was determined to be apparently 1.5×10^4 by SEC calibrated with P2VPs having narrow molecular weight distributions while those for L-1, L-2 (purified), and L-3 were 1.6×10^4, 1.3×10^4, and 1.1×10^4, respectively.

Pyrolysis−Gas Chromatography/Mass Spectrometry. A microfurnace pyrolyzer (Frontier Lab PY2010D) was directly attached to a gas chromatograph (Hewlett-Packard 5890A) equipped with a flame ionization detector (FID) and a high-resolution fused-silica capillary column (Hewlett-Packard Ultra 1, 0.2 mm i.d. × 50 m long) coated with immobilized dimethylsiloxane (0.33 μm thick). About 0.3 mg of the sample was pyrolyzed at 650 °C under a flow of helium carrier gas (80 mL/min) which was reduced to 1.1 mL/min at the capillary column by a splitter. The column temperature was programmed from 50 to 290 °C at a rate of 5 °C/min and then held at 290 °C. The peak identification of the pyrogram was mostly performed by using the Py-GC system directly coupled with a quadrupole mass spectrometer (Py-GC/MS) with electron impact (EI) ionization source at 70 eV (JEOL AM-II 150).

Results and Discussion

Figure 2 shows the pyrogram of the fractionated P2VP sample, R-1, observed by the Py-GC at 650 °C. The characteristic degradation products are 2VP monomer, dimer, and trimer, of which the relative peak intensity among the total is about 80%, 10%, and 3%, respectively. These main products that are mostly associated with the main chain of the molecule do not provide any good information about the ring structure at all. According to the anticipated ring structure, however, the possible smallest characteristic fragments that reflect the coupling moiety in the cyclic P2VP, if any, should be observed in the trimer region because the coupling agent combined with two 2VP units in both sides might yield a hybrid trimer containing three aromatic rings of which the molecular weight is to be very close to the 2VP trimer with three aromatic rings. Therefore, the trimer region is focused on in the following discussion. As shown in Figure 2, the expanded pyrogram in the trimer region consists of a number of peaks in addition to the strongest 2VP trimer (VVV).

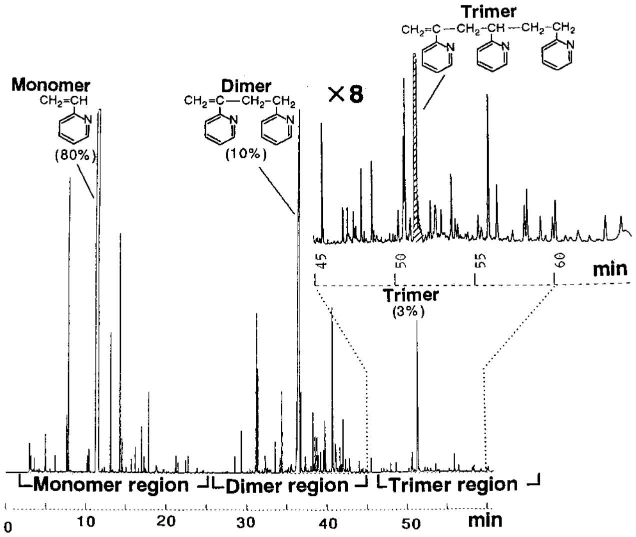

Figure 2. Pyrogram of poly(2-vinylpyridine) [P2VP] containing cyclic polymer fraction (sample R-1) at 650 °C.

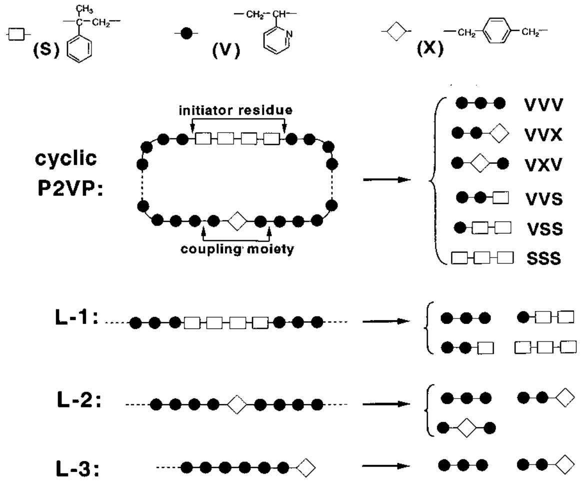

Figure 3. Possible trimer structure formed from cyclic poly(2-vinylpyridine) [P2VP] and model linear P2VP (L-1 to L-3).

Here three kinds of model linear P2VP (L-1, L-2, and L-3) were also used in order to comparatively discriminate the characteristic fragments which reflect the coupling moiety in the cyclic P2VP from the other many degradation products observed in the pyrogram. Figure 3 illustrates the possible trimer structures formed from the cyclic P2VP and the model linear P2VPs (L-1, L-2, and L-3), where 2VP, α-methylstyrene, and *p*-xylene units are abbreviated as V, S, and X, respectively. The possible degradation products from R-1 in the trimer region should comprise the fragments containing the residue of the initiator (SSS, VSS, and VVS) and those containing the moiety of the coupling agent (VVX) and (VXV) as well as the strongest 2VP trimer (VVV). On the other hand, as was illustrated in Figure 3, L-1, L-2, and L-3 should yield the respective characteristic trimers corresponding to the original molecular structures. Therefore, when the retention data of the peaks in the trimer region for L-1, L-2, and L-3 are carefully compared with each other, the possible candidates for the

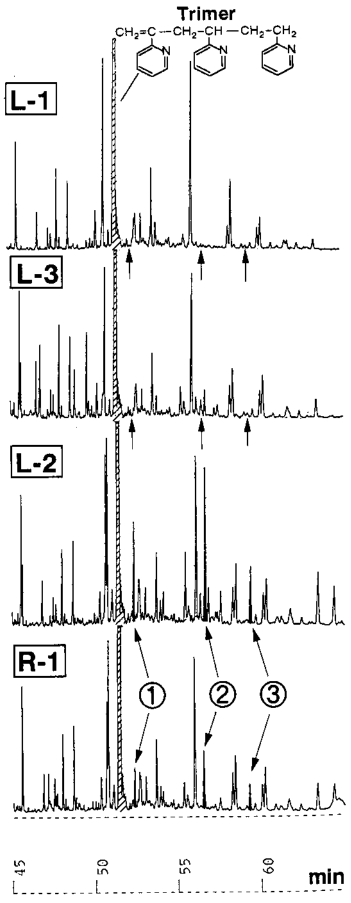

Figure 4. Detailed pyrograms in the trimer region of poly(2-vinylpyridine) [P2VP] containing cyclic polymer fraction (sample R-1) and model linear P2VP (L-1 to L-3).

key trimers of VXV which might reflect the coupling moiety in the ring polymer can logically be discriminated as follows.

Figure 4 shows the observed partial pyrograms in the trimer region for L-1, L-2, L-3, and R-1. The entire pyrograms of R-1 and the model linear P2VPs were almost identical, reflecting basically the same decomposition pathways due to their sufficiently large molecular weight over "a level of stabilization" which is to be around $M_n \sim 10^4$.[13] As shown in Figure 5, only some minor differences are observed around the trimer region which should be attributed to the specific microstructures such as the coupling moiety and initiator residue. The trimers which are observed on the pyrogram of L-2 but are missing on that of L-3 can be the candidates of VXV. These, however, might have the same retention times by chance as those of the other trimers including S unit such as VVS, VSS, and SSS, of which the contribution, if any, can easily be eliminated by comparing with the pyrogram of L-1. By this logical comparison of the pyrograms of the three model polymers (L-1, L-2, and L-3), it was deduced that the peaks 1, 2, and 3 appearing on the pyrogram of L-2 should be attributed to the peaks of the key trimers of VXV.

Then, by considering the deduction process mentioned above, the mass spectra of those three peaks (1, 2, and 3) were carefully interpreted. Figure 5 shows the observed EI mass spectra for the peaks 1, 2, and 3. The spectrum of the peak 1 indicates the M^+ ion at m/z 300 and fragment peaks at m/z 208 and 194. That of the peak 2 indicates the same M^+ ion at m/z 300 and the base peak at m/z 285 and a fragment peak at m/z 194.

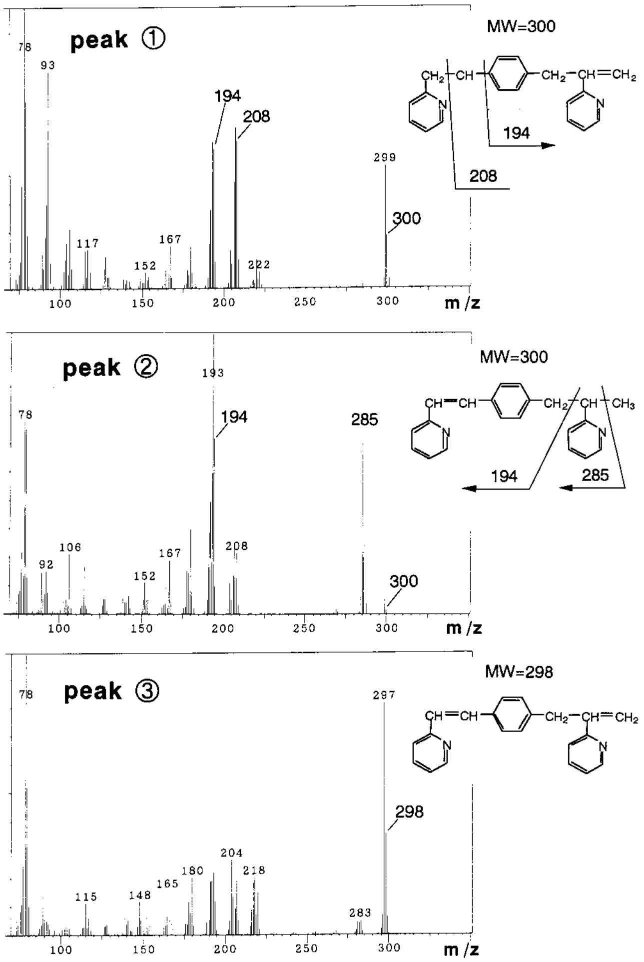

Figure 5. Mass spectra of the products reflecting the coupling moiety observed in the trimer region.

And that of the peak 3 indicates the M^+ ion at m/z 298. As was expected, the possible structural formulas of the three peaks thus estimated shown in Figure 5 have the common basic structure as VXV.

As shown in Figure 4, the specific peaks, 1, 2, and 3 are also clearly observed in the pyrogram of R-1. Therefore, it can be unequivocally concluded that R-1 should include a certain amount of the polymers with the anticipated ring structure illustrated in Figure 1. Here, it can be empirically estimated that about 30% of the fractionated P2VP sample (R-1) should have the ring structure by comparing the relative intensities of the specific peaks 1, 2, and 3 between R-1 and L-2, taking the following conditions into consideration: (1) each molecule of L-2 comprises one coupling moiety, and (2) R-1 and L-2 have almost comparable M_n, 1.5×10^4 and 1.3×10^4, respectively. In addition, the formation probabilities of the specific products from the coupling moiety was regarded to be equivalent for both the cyclic P2VP and the linear model L-2.

The amounts of the fraction with the ring structure might change depending on the preparative and fractionation conditions. The isolation of highly pure cyclic polymers and their characterization of chemical and physical properties are currently under investigation.

Acknowledgment. Financial support by the Grant-in-Aid for Scientific Research (A) (09305056 and 11355033) and (B) (09555262) of the Japan Society for the Promotion of Science (JSPS) and by a Grant from the "Research for the Future" Program of JSPS (JSPS-RFTF, 96R11601) is gratefully acknowledged.

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MA981921L