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Determination of Free-Radical Propagation Rate Coefficient of *N*-Vinylindole by the Pulsed-Laser Polymerization Method

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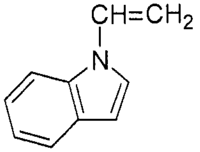
Summary

The pulsed-laser polymerization method was applied to determine the propagation rate constant k_p of *N*-vinylindole (VI), and the Arrhenius parameters were evaluated in the range of 30–70 °C. One of the characteristics of the VI monomer was its low activation energy (17.5 kJ mol^{-1}) compared with other vinyl monomers, indicating that the propagating radical has a high reactivity. Although the reaction rate constant $k_p = 86$ L mol^{-1} s^{-1} at 30 °C was relatively small and similar to that of styrene, the *Q*-value and the products of photochemical reactions suggested again that it has a higher reactivity than styrene monomer. This property of VI radical probably gives rise to high termination probability and the cyclic structure at the chain end of the linear polymer.

Introduction

Recently, poly(*N*-vinylindole) (PVI) has attracted much attention as a novel photorefractive polymer superior to the famous photoconductive polymer, poly(*N*-vinylcarbazole) (PVCZ), because of having a lower glass transition temperature, while keeping a good photoconductivity due to the low ionization potential of the pendant indole unit [1]. Therefore, PVI is a potential candidate of functional polymers. However, from the standpoint of polymer synthesis, only a few articles have been published so far [2–5]; e.g., Priola *et al.* reported polymerization of *N*-vinylindole (VI) with radical and cationic initiators [4]. Although they obtained low molecular weight (M_w) linear polymers, ^{13}C NMR spectroscopy indicated the presence of cyclic indoline units in the chemical structure of PVI, suggesting a back-biting attack of



Scheme 1. The monomer structure of *N*-vinylindole.

propagating species to the 2-position of the indole ring in the radical polymerization and to the 3-position in the cationic polymerization. Brustolin *et al.* reported successful preparation of high-M_w polymers from a series of VI derivatives with radical and cationic initiators in some specific solvents and concentrations [5]. These results suggest the difficulty of kinetic studies on VI systems since the side reactions tend to disturb the quantitative evaluation of the rate constants related to the linear propagation reaction. Actually, the propagation rate coefficient (k_p) has not been reported for the VI monomer, to our best knowledge.

In the current work, we determined the k_p of VI using the pulsed-laser polymerization (PLP) method, a recently developed technique reliable for determining the propagation rate constant, k_p, of radical polymerizations, and the use of which has been recommended by the IUPAC working party on "Radical Polymerization Kinetics and Processes" [6–12]. Thanks to the nice combination of the efficient photo-initiation by a pulsed-laser system and the exact M_w measurement by size exclusion chromatography (SEC), the propagation rate constants of many vinyl monomers have been unambiguously determined without any model assumptions. We have already reported the rate constants for *N*-vinylcarbazole (VCZ), which is one of the *N*-substituted vinyl aromatic monomers like VI, and discussed the wide applicability of the PLP method to various kinds of monomers [13]. As mentioned above, the polymerization of VI is our next research object from both views of polymer synthesis and functions. This paper presents the exact propagation rate constant of VI and its characteristics in comparison with some important vinyl monomers.

Experimental

Materials

Indole (Nacalai Tesque) was purified by repeated recrystallization. To a solution of indole (35 g) in heptane (530 mL) was added potassium hydride (35 wt%, 27 g), and the suspended solution was stirred and refluxed for 5 h, yielding indole potassium salt. The salt was filtered out and dried *in vacuo*. Ethylene oxide was added to a benzene solution of indole potassium salt in N_2 atmosphere. After the solution was washed with water, benzene was removed by distillation. The viscous product of *N*-hydroxyethylindole was distilled with KOH (7 g) under a reduced pressure (6.0 mmHg / 95–113 °C), and the crude product was again distilled at a reduced pressure (4.0 mmHg / 94–96 °C), yielding white needle-like crystals of VI (10 g, yield: 23.4 %). $n_d^{40} = 1.62$, $d_{40}^{40} = 1.05$, m.p. = 28.2 °C. ^{1}H NMR ($CDCl_3$, δ, ppm) 4.73 (d, 2H, C=CH_2), 5.15 (d, 1H, *H*C=C), 6.60 (d, 2H, aromatic *H*), 7.10–7.63 (m, 4H, aromatic *H*).

Measurements

UV and visible absorption spectra were recorded with a Hitachi U-3500 spectrophotometer. The PLP experiment was performed for neat VI containing 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (Irgacure 369) (Ciba Geigy) as a photoinitiator at the concentration of 2 mmol L^{-1}. The monomer in a glass cell was bubbled with argon for 10 min. Pulsed-laser experiments were carried out using a 351-nm pulse light of a XeF excimer laser (Lambda Physik, EMG 101 MSC, a pulse energy of 60 mJ/pulse, a pulse width of 18 ns, a pulse repetition rate of 10 Hz (t_0 = 0.1 s)). The number of pulses was adjusted so that the conversion did not exceed 3% of the monomer. The temperature was kept constant within ± 0.5 °C during the reaction. After polymerization, the molecular weight distribution (MWD) was analyzed by a high-speed liquid chromatography system, HLC-802UR (Tohso Co. Ltd.), equipped with a column (Tohso, TSK-GEL, G4000HHR × 2) and a differential refractometer. Tetrahydrofuran (THF) was used as the eluent, and pumped at a constant flow of 0.8 mL min^{-1}. The calibration of SEC was done first by the narrow MWD polystyrene standard (Tohso), and the M_w value was corrected according to the M_w of narrow-MWD PVI, whose absolute M_w was determined by a matrix-assisted laser-desorption ionization time-of-flight mass spectrometer (Bruker Daltonics, Inc., BIFLEX III).

PLP

The intense pulsed laser light decomposes the photoinitiator, resulting in periodic generation of a large amount of radicals. Let us consider the chain propagation of monomers, which is initiated at the moment of a given pulse, and then terminated by radicals produced by one of the following pulses. Therefore, the degree of polymerization L_i of the polymer terminated by the i-th pulse after the initiating pulse, will be given by

$$L_i = i\,k_p\,[M]\,t_0 \tag{1}$$

where $[M]$ is the monomer concentration, t_0 is the dark period between two subsequent pulses, and i is an integer. Therefore, the value L_i indicates how many monomers participate in the propagation reaction within the defined time interval of pulsed irradiation. Consequently, the MWD of polymers thus obtained shows characteristic peaks on the SEC. Olaj *et al.* suggested that the inflection point at the low molecular weight side of each peak is the best measure of L_i [6]. MWD was analyzed by Hutchinson's method [7]. Once L_i is determined, we are able to evaluate k_p from Eq. 1, in which $[M]$ and t_0 are explicit parameters known beforehand by the experimental conditions.

Results and discussion

Figure 1 shows the absorption spectra of VI (7.33 mol L^{-1}, solid line) and Irgacure 369 (2 mmol L^{-1}, broken line) in a 1-mm cell. Although the VI absorption remained slightly at the wavelength of laser light, 351 nm, the polymerization did not take place when the system was irradiated in the absence of Irgacure 369. Taking into account the large absorbance of Irgacure 369 at the excitation wavelength, it is safely said that the polymerization started with radical species produced by decomposition of Irgacure 369, which were assigned to benzoyl and aminoalkyl radicals by Desorbry *et al.* [14].

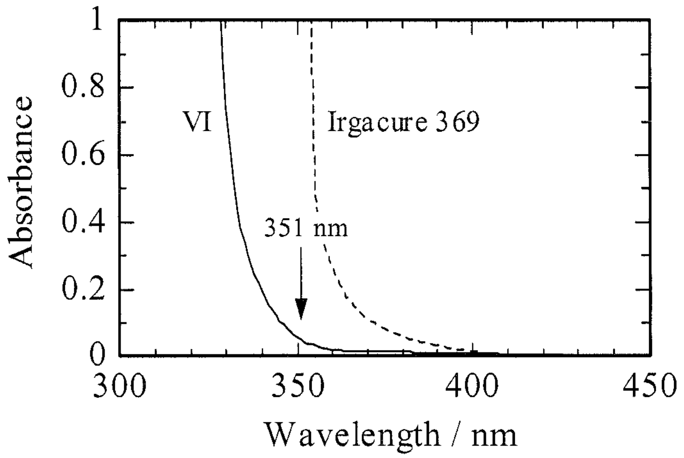


Figure 1. Absorption spectra of VI (solid line) and Irgacure 369 (broken line).

Figure 2 shows a typical example of MWD curves and its first derivative measured by SEC, where the fraction of polymer w was expressed as a function of log M_w. Taking the first derivative of $d[w(\log M_w)]/d(\log M_w)$, obvious maxima appeared on the chromatogram at the inflection point of each MWD peak. These maxima represent L_i; in this example, L_1 and L_2 were observed as the first and the second peaks. It should be noted that the M_w of L_2 is twice as large as that of L_1. These experiments were performed in a wide range of temperatures, 30–70 °C.

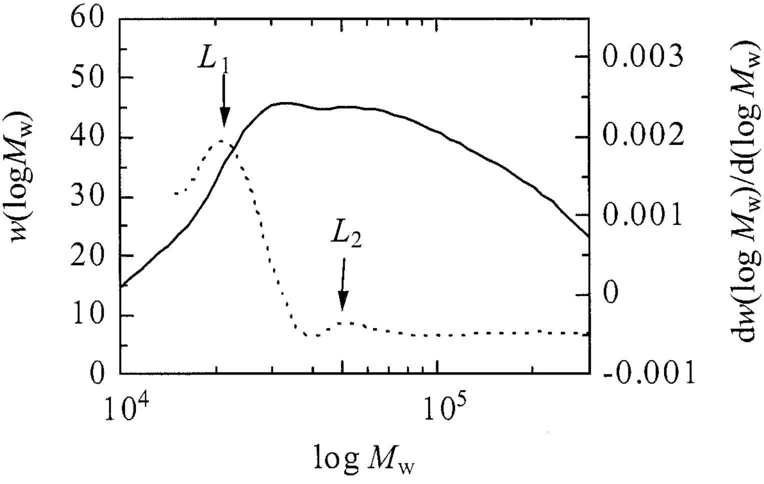


Figure 2. Molecular weight distribution $w(\log M_w)$ (solid line) of the polymer formed in PLP experiment for VI [temperature: 70 °C; $t_0 = 0.1$ s; VI (bulk); Irgacure 369 (2 mmol L^{-1})] and the first derivative $dw(\log M_w)/d(\log M_w)$ (broken line) measured by SEC. The inflection points of the MWD curve are shown as L_i.

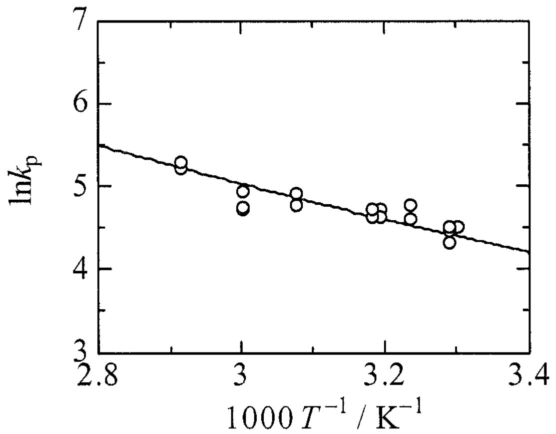


Figure 3. Arrhenius plot for the VI propagation rate constants determined by PLP.

According to Eq. 1, the L_1 value was converted to k_p and the $\ln k_p$ was plotted in the following linear form of the Arrhenius equation.

$$\ln k_p = \ln A - E_A / RT \qquad (2)$$

Figure 3 shows the plots for the VI propagation rate constants determined by the PLP method at several temperatures. The solid line represents the least square fitting, which can be written in the following rate equation:

$$k_p = 8.49\times10^4 \exp\left(\frac{-17.5\ \mathrm{kJ\,mol^{-1}}}{RT}\right) \qquad \left(\mathrm{L\ mol^{-1}\ s^{-1}}\right) \qquad (3)$$

where the Arrhenius parameters were obtained as $A = 8.49 \times 10^4$ L mol^{-1} s^{-1}, E_A = 17.5 kJ mol^{-1} and the value of k_p at 30 °C was found to be 86 L mol^{-1} s^{-1}. The PLP method gives a direct measurement of k_p, independent of the termination rate constant, k_t. This is a great advantage for analyzing the kinetics of monomers having a large k_t, such as VI and vinyl acetate, because conventional kinetic determinations must rely on the ratio of k_p/k_t [15].

Table 1. Propagation rate constants and the related parameters for some important vinyl monomers.

Monomer	k_p (L mol^{-1} s^{-1})	A (L mol^{-1} s^{-1})	E_A (kJ mol^{-1})	Q	e	Ref
VI	86	8.49×10^4	17.5	0.53	−1.30	this work
Styrene	112	4.30×10^7	32.5	1.0	−0.8	11
MMA	360	2.39×10^6	22.2	0.74	0.40	12
VCZ	4200	2.20×10^8	27.4	0.26	−1.29	13

It is instructive to compare the propagation rate parameters with other reported values. Table 1 lists those for some important monomers previously reported by our laboratory [13] and other researchers [11,12]. A marked feature of VI exists in the low activation energy E_A, suggesting that the propagating VI radical possesses high reactivity. Generally, the reactivity of radicals has been explained in terms of the *Q*-value of monomers as a measure of resonance effect on stabilization energy. To discuss the characteristics of VI monomer, the *Q*–*e* values were determined by copolymerization of styrene and VI. Figure 4 shows the monomer-copolymer composition curve of VI(1) and styrene(2) (r_1 = 0.276, r_2 = 2.82) with experimental data. The *Q*–*e* values of VI derived from r_1 and r_2 thus obtained are listed in Table 1. Compared with the styrene standard, the *Q*-value of VI was much smaller, indicating that little stabilization energy is available from the pendant indole ring, resulting in the higher reactivity of VI. In comparison with VCZ, the *Q*-value of VI is larger than that of VCZ. This result supports that the reactivity of VI is much lower than that of VCZ.

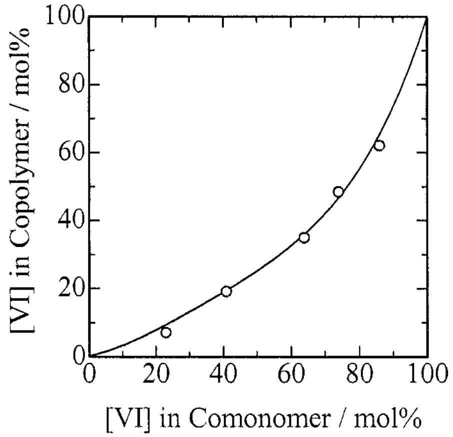
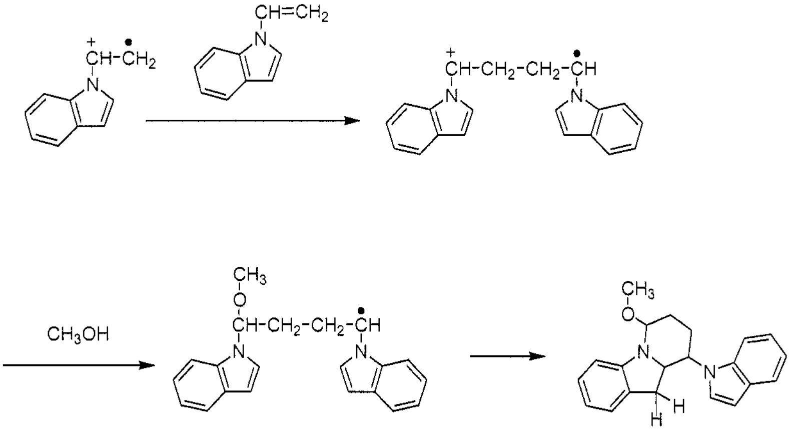


Figure 4. Theoretical curve of VI–St copolymer composition curve calculated from the monomer reactivity ratios (r_1 = 0.276, r_2 = 2.82).

The reactivity of VI radical was also confirmed in the photochemical dimerization reaction. When a solution of VI was irradiated in the presence of an electron acceptor, the following reaction took place in MeOH.



Scheme 2. The scheme of photochemical reaction in MeOH.

The dimer radical cation was produced as an intermediate, and the cationic end was captured by methoxy addition from the solvent. The residual radical at the counter end attacked the adjacent indole pendant, yielding 4-(1-indolyl)-2,3-dihydro-1-methoxypyridino[1,6-a]-indole as a major product. This may be a typical example of the back-biting reactions for the propagating VI radicals. Even if the same experiments were performed for styrene systems, no cyclic product was obtained besides a linear dimeric styrene capped with a methoxy substituent at the one end [16,17].

Regardless of the high reactivity of radicals, VI showed a propagation rate constant as small as that of the styrene monomer, mainly due to the small frequency factor A. Unfortunately, there is no reliable explanation for this cause at the moment. Further experiments under various conditions, e.g., at lower temperatures or at shorter t_0 of PLP, are needed to clarify this issue.

Conclusion

The propagation rate constant k_p of VI was successfully determined by the PLP technique in the range of 30–70 °C. Although the previous works suggested some hindrance for the kinetic analyses as a result of the high termination probability of VI radical, the MWD curves with a characteristic maximum could be observed on SEC measurements. The Arrhenius parameters were evaluated by least-squares fitting: $A = 8.49 \times 10^4$ L mol^{-1}s^{-1} and $E_A = 17.5$ kJ mol^{-1}. The small activation energy seems to be a particular feature of the VI monomer, indicating the high reactivity of propagation radicals. This result is in good agreement with the photochemical reactions of VI. However, the origin of the small rate constant of $k_p = 86$ L mol^{-1} s^{-1} at 30 °C still remains as a future research subject.

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