

SHORT COMMUNICATIONS

**Radical Propagation Rate Coefficient of *N*-Vinylcarbazole Measured by Pulsed-Laser Polymerization**

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The radical and cationic polymerization of *N*-vinylcarbazole (VCZ) has been extensively studied.<sup>1,2</sup> In the polymerization kinetics, it is important to determine propagation rate constants ( $k_p$ ). North *et al.*<sup>3</sup> measured propagation rate constants for radical polymerization of VCZ by using the rotating sector-dilatometry method and reported the value of  $k_p = 13 \text{ L mol}^{-1} \text{ s}^{-1}$  at 30°C in tetrahydrofuran (THF), which is listed in “Polymer Handbook.”<sup>4</sup> We reported the value of  $k_p = 930 \text{ L mol}^{-1} \text{ s}^{-1}$  at 30°C in benzene by the same method.<sup>5</sup> There was a big difference between the two values. Recently, Olaj and coworkers<sup>6</sup> developed the pulsed-laser polymerization (PLP) technique by which the propagation rate constant of radical polymerization can be evaluated accurately. In the present study, we reinvestigated the propagation rate constant of radical polymerization of VCZ by the PLP technique and found a rather large value different from the previous ones:  $k_p = 4.11 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$ ,  $E_a = 28.8 \text{ kJ mol}^{-1}$  at 30°C in benzene.

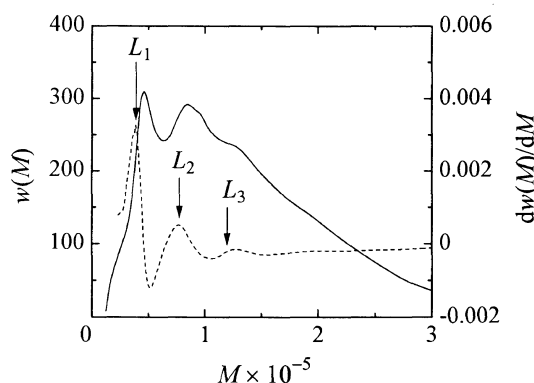
The PLP technique has been described in many papers<sup>7,8</sup> and has been recommended for use by an IUPAC working party.<sup>9,10</sup> Olaj and coworkers showed that the kinetic chain length,  $L$ , can be expressed by eq 1.

$$L = k_p[M]t_0 \quad (1)$$

where  $[M]$  is the monomer concentration.  $t_0$  is the time (dark time) between pulses. The molecular weight distribution (MWD) was measured by size exclusion chromatography (SEC). The MWD analysis was based upon universal calibration using narrow MWD polystyrene standards and Mark–Houwink–Sakurada coefficients. In this study, we used 2-benzyl-2-dimethylamino-1-(4-morpholinophenyl)-butanone-1 (Irgacure 369) (Ciba Geigy) as a photoinitiator which has an absorption tail up to *ca.* 410 nm.

Figure 1 shows the molecular weight distribution and its derivative curve for the sample after irradiation of 10 Hz of light 351 nm to the system: VCZ ( $0.5 \text{ mol L}^{-1}$ ), Irgacure 369 ( $2 \times 10^{-3} \text{ mol L}^{-1}$ ) at 30°C in benzene solvent. In the absence of the photoinitiator, the photopolymerization of VCZ did not take place under this condition. The kinetic chain length ( $L$ ) was determined from the inflection point which was read off as a maximum in the molecular weight distribution

derivative. The  $k_p$  value was determined from this  $L$  using eq 1. Table I shows the values which we analyzed from the first peak  $L_1$  and the second peak  $L_2$  of the curve. The relationship between the first peak and the second peak is  $L_2 = 2 \times L_1$  and the relationship was well held in this experiment. The frequency of light pulse was changed from 5 Hz to 30 Hz. With the increase of frequency, the SEC curves shifted to the lower molecular weight side. In other words, the shift of  $L_1$  was proportional to the time  $t_0$  and  $L_1$  gave a constant  $k_p$  value. The propagation rate constants  $k_p$ 's measured in the range of 30–70°C were treated by the least squares method and the relationship of  $k_p [\text{L mol}^{-1} \text{ s}^{-1}] = 3.72 \times 10^8 \exp(-28.8 \text{ kJ mol}^{-1}/RT)$  was obtained in benzene solvent: the value calculated from the equation is  $k_p = 4.11 \times 10^3 \text{ L mol}^{-1} \text{ s}^{-1}$  at 30°C. The discrepancy between the previous and the present values suggests that the rotating sector-dilatometry method is not accurate enough to determine the rates of solution polymerization, and that there was no clear-cut radical photoinitiator for VCZ monomer.<sup>11</sup> We examined the reliability of our technique by mea-



**Figure 1.** Molecular weight distribution (solid line) and its derivative (dotted line) for the polymer formed in a pulsed-laser polymerization of VCZ at 30°C in benzene solvent. Laser repetition rate, 10 Hz.

**Table I.** Inflection point MW, kinetic chain length  $L$ , and propagation rate coefficient  $k_p$

	Inflection point MW ( $\times 10^3$ )	$L$	$k_p (\times 10^3, \text{ L mol}^{-1} \text{ s}^{-1})$
First	38.8	201	4.02
Second	77.4	401	4.01
Third	118.3	612	4.08

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suring the  $k_p$  of bulk styrene, then our result was in good agreement with Manders' result.<sup>12</sup> The details will be reported shortly.

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