

## Living Anionic Polymerization of 3-Vinylpyrene with Sodium-Naphthalene Complex

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With the cationic, radical and Ziegler-Natta catalysts we have already succeeded in polymerizing 3-vinylpyrene (3-VP), a vinyl monomer having the largest aromatic group hitherto known.<sup>1)</sup> We have now found that the living anionic polymeriza-

tion of this monomer is possible if the monomer is purified finally by sublimation in high vacuum and used without being exposed to air.

Polymerization was carried out by using high vacuum technique, and by adding the tetrahydrofuran (THF) solution of the sublimed monomer into the THF solution of the initiator, sodium-naphthalene, at room temperature. Typical results are shown in Table I.

On addition of the monomer solution (pale yellow color), the green color of the solution of the initiator changed immediately to blue, showing absorption maximum at 620 m $\mu$  (Fig. 1). This band is attributed to the absorption of the living poly-3-vinylpyrene (PVP) for the following reasons. (1) The wavelengths of the absorption peaks of the living polystyrene,<sup>2)</sup> polyvinylbiphenyl,<sup>3)</sup> and poly-1-vinylnaphthalene<sup>4)</sup> are 342, 405 and 558 m $\mu$ , respectively. It seems, therefore, reasonable that the spectrum of the living PVP shows a maximum at 620 m $\mu$ . (2) The color of the solution of the living PVP does not change appreciably by further addition of the monomer solution, while the total polymer yield increases considerably with the simultaneous increase of the intrinsic viscosity of the isolated polymer, as shown in Table I.

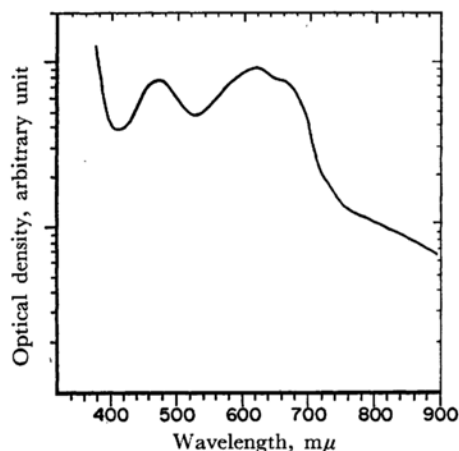


Fig. 1. Absorption spectrum of living PVP in THF at room temperature.

TABLE I. POLYMERIZATION OF 3-VINYLPYRENE

The 1st addition of the monomer g (mol $\times 10^4$ )	The 2nd addition of the monomer g (mol $\times 10^4$ )	Initiator (mol $\times 10^5$ )	Yield g	Softening range $^{\circ}\text{C}$	Intrinsic viscosity*
0.18 (7.9)	—	1.0	0.17	281 <	0.23
0.16 (7.0)	0.15 (6.6)	0.9	0.28	300 <	0.31

\* in THF at 25 $^{\circ}\text{C}$ .

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