

## Chain Transfer to Toluene in *n*-Butyl-lithium Initiated Polymerization of Styrene

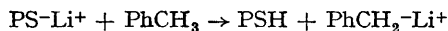
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VISCOSITY measurements indicate that chain transfer to the solvent, toluene, occurs in the anionic polymerization of styrene with sodium as the counter-ion.<sup>1,2</sup> On the other hand, viscosity measurements indicated that the polymerization proceeded without chain transfer when lithium was the counter-ion.<sup>1</sup>

Our observation of broader molecular weight distributions than anticipated in the *n*-butyl-lithium initiated polymerization of styrene in toluene led us to believe that chain transfer occurs with the lithium counter-ion also. This was proved by conducting the polymerization in [<sup>14</sup>C]toluene and isolating a radioactive polymer. This technique is more sensitive to measuring small chain-transfer coefficients than are viscosity measurements.

The probable mechanism for chain transfer to toluene in an anionic polymerization is an acid-base exchange between the growing chain and toluene, followed by initiation of a new chain by benzyl-lithium. Each transfer step incorporates one molecule of toluene into



the polymer. The rate of reaction of *n*-butyl-lithium with toluene (as measured by butane evolution) was found to be much smaller than the initiation rate reported by Hsieh.<sup>3</sup> Therefore incorporation of toluene into the polymer through reaction with the initiator is negligible.

The polymerizations were conducted in much the same manner as reported by Brooks<sup>1</sup> only using *n*-butyl-lithium (0.5 M in benzene, Foote Mineral) as initiator and [<sup>14</sup>C]toluene ( $1.93 \times 10^5$  d.p.m./ml.) as solvent. A polymer sample of constant activity was obtained by repeated evaporation of solvent from a xylene solution of the polymer. Molecular weights and molecular-weight distributions were determined from ultracentrifuge data.<sup>4</sup> Chain-transfer coefficients were calculated from the integrated form of expression for the ratio of the rate of chain transfer to the rate of propagation

$$\frac{T}{\bar{P}} = -C_s \frac{[S]}{[M_1]x} \ln(1-x)$$

where  $T$  = moles of toluene/g./polymer,  $\bar{P}$  = moles monomer polymerized/g. polymer,  $C_s$  = chain transfer coefficient (ratio of transfer to

TABLE

*Effect of temperature on chain-transfer activity of toluene*

Temp.	d.p.m.	$\ln(1-x)/x$	$M_n/x \times 10^{-5}$	$M_w/M_n$	$C_s \times 10^5$
62	54.8	2.24	103.6	1.14	1.64
72	60.0	2.58	105.0	1.11	1.56
87	101	5.12	105.5	1.12	1.32
100	159	6.28	110.0	1.12	1.69

Styrene: 11.3 g. in 100 ml. of solution; Bu<sup>n</sup>Li: 0.20 ml. of 0.53 M; Theoretical mol. wt. =  $1.07 \times 10^5$ .

propagation rate constants),  $S$  = solvent concentration,  $M_1$  = initial monomer concentration, and  $x$  = the degree of conversion.

The data in the Table show that  $C_s$  is independent of the temperature. Although at first this result appears surprising, it is not unreasonable considering that the difference in activation energies for addition to 1,1-diphenylethylene and proton abstraction from fluorene by n-butyllithium is less than 1 kcal.<sup>5</sup> The molecular weight and molecular-weight distribution are also independent of temperature which is in agreement with this result.

The effect of chain transfer on molecular-weight distribution only becomes measurable at higher molecular weights as seen in the Figure. The observed molecular weights appear to vary randomly about the molecular weight calculated from  $[g. \text{ polymer}]/[\text{moles initiator}]$ . A decrease in the observed molecular weight relative to the calculated value is expected to accompany the increase in broadening. It is believed this trend is masked by the experimental error in measuring the small amount of effective initiator required to produce these high molecular weights.

As a consequence of the logarithmic dependence of chain transfer on conversion, the growing chains are largely present as oligomers at very high conversion and therefore are of little utility in macromolecular synthesis.

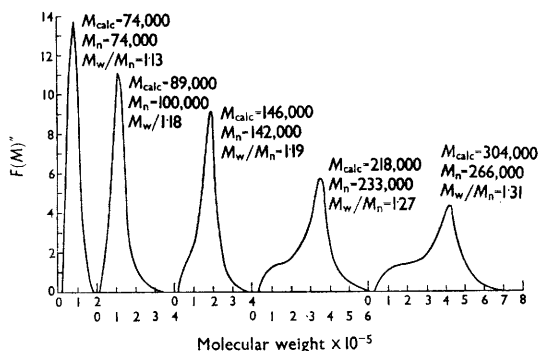


FIGURE. The observed molecular weights and molecular-weight distributions of polystyrene at varying calculated molecular weights.

(Received, September 15th, 1967; Com. 990.)

<sup>1</sup> B. W. Brooks, *Chem. Comm.*, 1967, 68.

<sup>2</sup> F. M. Brower and H. W. McCormick, *J. Polymer Sci., Part A, General Papers*, 1963, **1**, 1749.

<sup>3</sup> H. L. Hsieh, *J. Polymer Sci., Part A, General Papers*, 1965, **3**, 163.

<sup>4</sup> H. W. McCormick, *J. Polymer Sci.*, 1959, **36**, 341.

<sup>5</sup> A. G. Evans, C. R. Gore, and N. H. Rees, *J. Chem. Soc.*, 1965, 5110.