

## Notes

### *Effect of Molecular Weight on Various TGA Methods in Polystyrene Degradation*

In the preceding article<sup>1</sup> we compared various methods of thermogravimetric analysis in case of polystyrene degradation using a 110,000 molecular weight sample. The reaction parameters were evaluated from common TG curves and the reaction was found to be of the first order with an average activation energy of 61.0 kcal/mol, though there were slight differences depending on the analytical methods used. We extended this study to check the effect of molecular weight, because this effect was emphasized by Kokta et al.<sup>2</sup>

#### RESULTS AND DISCUSSION

Main experimental conditions were the same those used in the previous paper<sup>1</sup>. The samples used and their corresponding molecular weight, both number and weight average values, are summarized in Table I. A representative result is shown in Fig. 1, where the TG curves for polystyrene samples with the different molecular weight are given. Several analytical methods were then applied to the experimental results. Figure 2 shows the relationship between activation energy and molecular weight thus obtained with the well-known Kokta's result<sup>2</sup> together.

Little or no dependence of the activation energy on molecular weight was found in the range of  $\bar{M}_n$  above  $10^5$  though the values change between 50 and 78 kcal/mol depending on the method em-

TABLE I  
Molecular Weights of Polystyrene Samples<sup>a</sup>

$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_w/\bar{M}_n$
$2.2 \times 10^3$	$2.42 \times 10^3$	1.10
$1.0 \times 10^4$	$1.06 \times 10^4$	1.06
$1.1 \times 10^5$	$1.17 \times 10^5$	1.06
$2.0 \times 10^6$	$2.60 \times 10^6$	1.30

<sup>a</sup> Samples were purchased from Pressure Chemical Co.

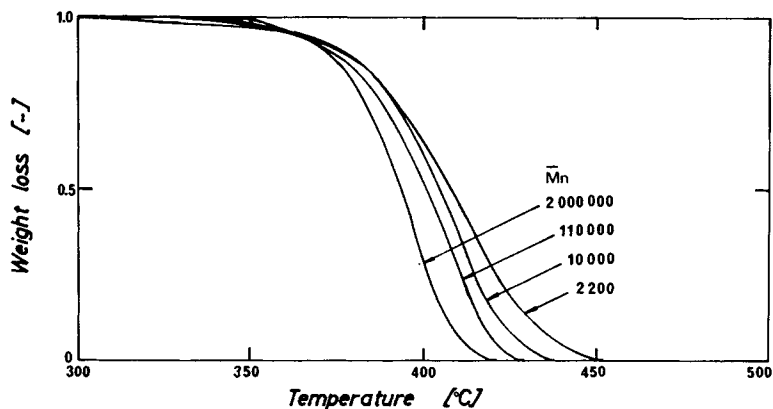


Fig. 1. TG curves for samples with different molecular weights.  $\beta = 10^\circ\text{C}/\text{min}$ ,  $w_0 = 5$  mg.

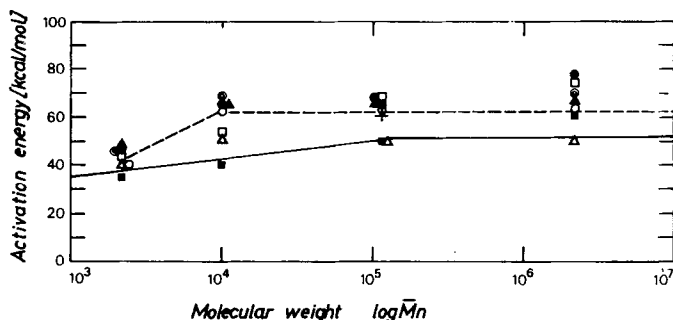


Fig. 2. Effect of molecular weight on activation energy. (●) Horowitz and Metzger, (■) Reich, (□) Reich and Levi, (Δ) Ozawa, (▲) Kissinger, (○) Freeman and Carroll, (+) Chatterjee, (⊙) Anderson and Freeman, (—) Kakta et al., (- - -) average. (All methods described in preceding article.<sup>1</sup>)

ployed. On the contrary, however, it was noted that the activation energy clearly decreases in accordance with Kokta's finding as the molecular weight becomes lower than  $10^4$ . Further examination will be made of the effects of sample weight as well as heating rate.

#### References

1. H. Nishizaki, K. Yoshida, and J. H. Wang, *J. Appl. Polym. Sci.*, **25**, 2869 (1980).
2. B. V. Kokta, J. L. Valade and W. N. Martin, *J. Appl. Polym. Sci.*, **17**, 1 (1973).

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