Polymer Bulletin 14, 259–264 (1985)

Polymer Bulletin

New Telechelic Polymers and Sequential Copolymers by Polyfunctional Initiator Transfer Agents (Inifers)

49. Extended Compositional Homogeneity Studies of Mono- and Multifunctional Polyisobutylenes Using the Kennedy-Smith Plot

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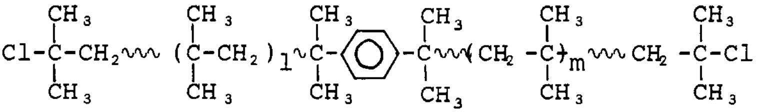
Summary

The Kennedy-Smith plot routinely used for the characterization of end-reactive (telechelic) polyisobutylenes has been recast to increase its accuracy and thus to increase its diagnostic value for the compositional analysis of telechelic polymers containing chromophores. A detailed error estimation is given. The plotting method and error limits are shown for representative mono-, di-, and tri-ended telechelic polyisobutylenes.

I. Introduction

GPC analysis by the use of dual detectors (i.e., instruments equipped with an RI and UV detector) provides valuable information as to the compositional homogeneity of polymer samples containing chromophores. Thus the height of the UV trace is proportional (k) to the number of chromophores (n) at a given elution volume: UV = k·n. Similarly, the height of the RI trace is proportional (K) to the weight fraction of the sample (N·M) at a given elution volume: RI = K·N·M, where N is the number of polymer molecules of M molecular weight.

The Kennedy-Smith method (1) makes use of the UV and RI traces produced by the GPC instrument. Figure 1 shows a set of UV and RI data obtained with α, ω-ditert.-chloropolyisopolyisobutylene:



$$Cl{-}\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2\sim\sim(\overset{CH_3}{\underset{CH_3}{C}}{-}CH_2)_l\sim\overset{CH_3}{\underset{CH_3}{C}}{-}C_6H_4{-}\overset{CH_3}{\underset{CH_3}{C}}\sim\sim(CH_2{-}\overset{CH_3}{\underset{CH_3}{C}})_m\sim\sim CH_2{-}\overset{CH_3}{\underset{CH_3}{C}}{-}Cl$$

(The synthesis has been described in ref. (2), sample XII/10). At every elution volume, i.e., along axis (x),

$$\frac{UV}{RI} = \frac{k}{K} \cdot \frac{n}{N \cdot M} .$$

By selecting a reference value, preferentially the maximum RI peak to minimize the experimental error, and by plotting

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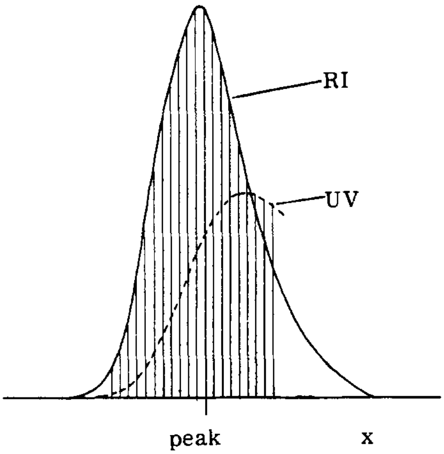
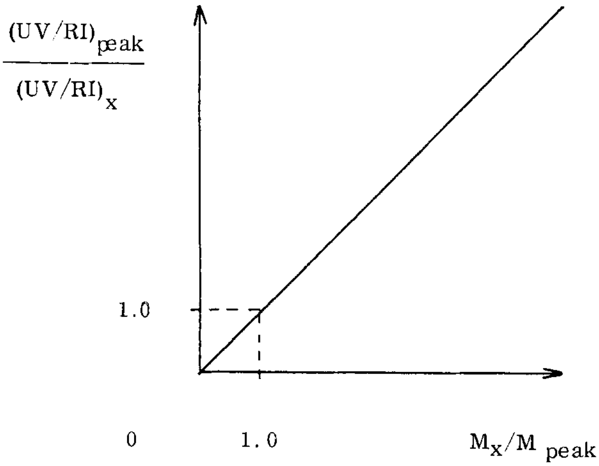
$$\left(\frac{UV}{RI}\right)_{peak}/\left(\frac{UV}{RI}\right)_{x} \quad \text{against} \quad \frac{M_x}{M_{peak}} \qquad (1)$$

Figure 1. The GPC Traces of Exp. XII/10 in ref.(2) for the Calculation of Kennedy-Smith Plot.



one must obtain a straight line with unity slope if every polymer molecule contains the same number of chromophore groups in every fraction along the elution volume axis. Figure 2 shows the Kennedy-Smith plot.

Figure 2. Kennedy-Smith Plot



This method is routinely used for the analysis of telechelic polyisobutylenes, in particular, to demonstrate that every chain contains the same number of chromophores along the distribution axis.

Using this method, however, sometimes it is difficult to decide whether the plot is in fact a straight line with unity slope. This is particularly the case with the experimental points closest to and farthest from the start (ascending part) of the RI and UV traces. These data points are difficult to asses experimentally and may contain large errors. To alleviate these potential problems and to render the Kennedy-Smith plot more accurate the variables have been modified. The principle of this linearization modification is the same as that used by Kelen and Tüdős to increase the accuracy of copolymerization reactivity ratio determinations (3,4).

II. The Modified Kennedy-Smith Plotting Method

According to the Kennedy-Smith plot (see above) the data points fall between 0 and infinity. The accuracy of the method can be improved by plotting

$$y = \frac{(UV/RI)_{peak}}{(UV/RI)_{peak} + (UV/RI)_x} \quad \text{versus} \quad x = \frac{M_x}{M_{peak} + M_x} \qquad (2)$$

in which case the data points will vary between 0 and 1.0.

III. Error Analysis

An error analysis has been carried out to help decide whether or not an experimental data point falls on the theoretical line of unity slope.

Since $y = f(UV_{peak}, UV_x, RI_{peak}, RI_x)$ and $x = f(M_p, M_x)$, the absolute errors of y and x, including the error limits of the variables, may be expressed, respectively, by the following equations:

$$|\delta y| = \sqrt{\left(\frac{\partial y}{\partial UV_p}\cdot\delta UV_p\right)^2 + \left(\frac{\partial y}{\partial UV_x}\,\delta UV_x\right)^2 + \left(\frac{\partial y}{\partial RI_p}\,\delta RI_p\right)^2 + \left(\frac{\partial y}{\partial RI_x}\,\delta RI_x\right)^2} \qquad (3)$$

$$|\delta x| = \sqrt{\left(\frac{\partial x}{\partial M_p}\,\delta M_p\right)^2 + \left(\frac{\partial x}{\partial M_x}\,\delta M_x\right)^2} \qquad (4)$$

Substituting y and x in eqs. (3) and (4) the relative errors of y and x are obtained:

$$\frac{\delta y}{y} = (1-y)\sqrt{\left(\frac{\delta UV_p}{UV_p}\right)^2 + \left(\frac{\delta RI_p}{RI_p}\right)^2 + \left(\frac{\delta UV_x}{UV_x}\right)^2 + \left(\frac{\delta RI_x}{RI_x}\right)^2} \qquad (5)$$

and

$$\frac{\delta x}{x} = (1-x)\sqrt{\left(\frac{\delta M_x}{M_x}\right)^2 + \left(\frac{\delta M_p}{M_p}\right)^2} \qquad (6)$$

IV. Demonstrating the Use of the Modified Kennedy-Smith Plot

The polymerization of isobutylene by the inifer method (1), be this by the use of an aromatic minifer, binifer or trinifer, must give rise to tert.-chlorine ended polyisobutylenes containing one aromatic residue (chromophore). Figures 3, 4 and 5 show modified Kennedy-Smith plots constructed for polymers obtained by the minifer (5), binifer (2) and trinifer (6) process, respectively. The figures also contain the error limits calculated by eqs. 5 and 6.

According to these data the agreement between the experimental points and theoretical line of 45 degrees (unity slope) is satisfactory indicating that every polymer molecule in the distribution (along the elution volume axis) contained the same number of chromophores i.e., one phenyl ring per chain. Evidently in these representative experiments the inifer method gave rise to compositionally homogeneous telechelic polymers.

Figure 3. Modified Kennedy-Smith Plot of α-Phenyl-ω-tert. chloro-PIB Prepared by the Minifer Technique (Sample: FDF1 Ref. (5))

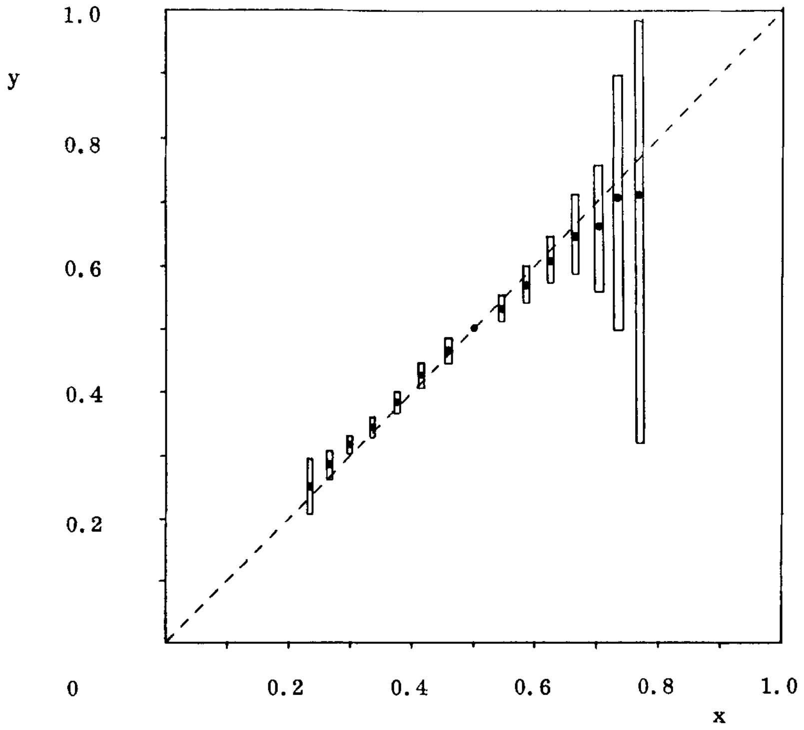


Figure 4. Modified Kennedy-Smith Plot of α,ω-di-tert.chloro PIB Prepared by the Binifer Technique (Sample: XII/10 Ref. (2))

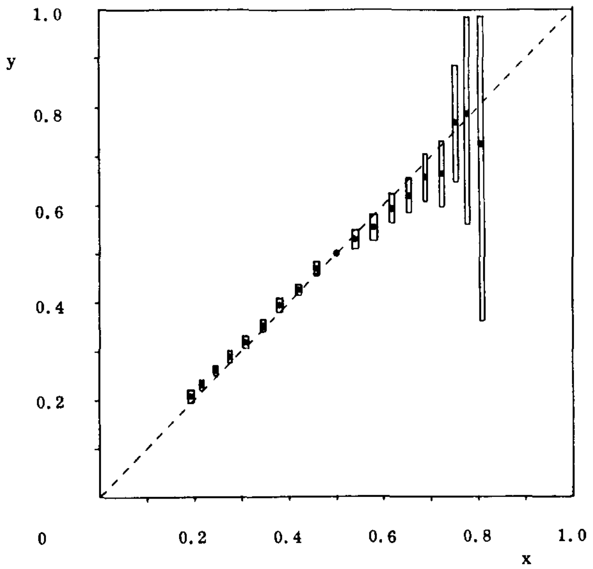
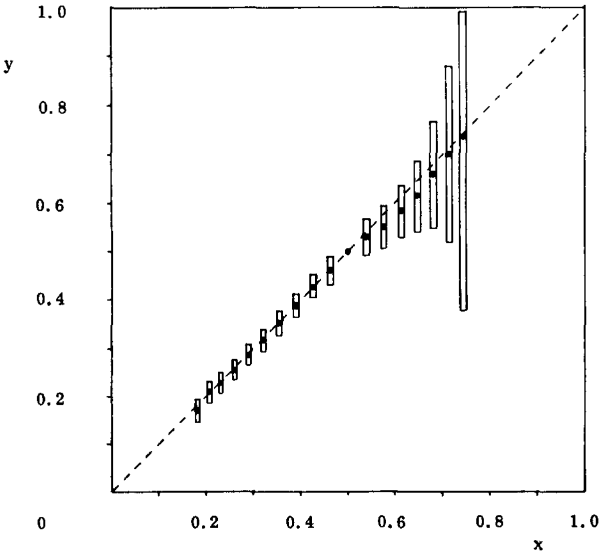


Figure 5. Modified Kennedy-Smith Plot of a Three-Arm Star PIB Carrying tert.-Chloro End Groups Prepared by the Trinifer Technique (Sample X/8 Ref. (6))



Acknowledgement. The author wishes to thank Dr. J. P. Kennedy for helpful comments and suggestions. Financial support by the National Science Foundation (Grant 84-18617) is gratefully acknowledged.

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Accepted September 24, 1985 *K*