

Macromer Copolymerization Reactivity Ratio Determined by GPC Analysis

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SUMMARY

In this paper is described a new method for determining copolymerization reactivity ratios r by using high resolution gel permeation chromatography. The system of monomers is a new one involving a macromer. Separation of each monomer, copolymer and solvent allows calculation of concentration of reactants and products, so as the copolymer molecular weight distribution.

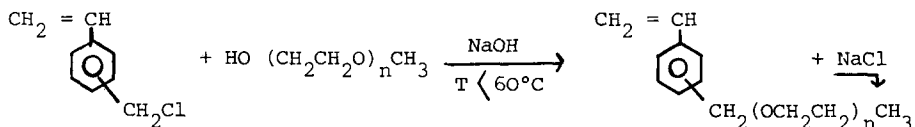
Three different methods were used to interpret copolymerization experiments, at various feed compositions, and in function of conversion, in minimizing errors on peak surface area. The conventional methods were used to calculate r and evaluate their accuracies.

INTRODUCTION

During copolymerization, the difference in values of the rate constants of each monomer has two main consequences, firstly a shift of monomer feed composition with conversion, and secondly, a particular microstructure both dependent on relative monomer concentration and reactivity ratios r . Then, the knowledge of r is of interest and may be determined by analysis of feed and/or copolymer at different feed compositions, or at different conversions, and applying 1 of the copolymerization equations. Analysis of the copolymer is valid only at low conversion, or by applying the integral form of the copolymerization equation at high conversion. In all cases, recovery and purification of the copolymers is necessary. Analysis of the feed composition has been facilitated with advent of gas chromatography, although there are some limitations in molar weight, volatility and thermal stability of the monomers. The method also fails when strong interaction occurs between stationary phase and monomer. For example, this situation is encountered when the monomer is a macromer, i.e. a polymer molecule with a polymerizable end-group. High performance liquid chromatography may solve such problems for moderate molar weight compounds; high resolution gel permeation chromatography¹⁾ (GPC or size exclusion S.E.C.) presents the same possibilities for reagents and moreover gives information on both amount and molar weight distribution of the copolymer²⁾. The separation of small species and accurate quantitative interpretations of the chromatograms are the main problems that were solved by combining several methods of measurements and data treatment to minimize errors. The original system studied here is (polyethoxy)-styrene - butylacrylate.

EXPERIMENTAL

- Reagents : Butylacrylate (BA) was from Fluka and used as it was.
 (Polyethoxy)styrene was obtained by condensation in alkaline medium of vinylbenzylchloride (VBC) and monomethylether of polyoxyethylene glycol ³⁾ (24 hrs)



VBC (Dow Chemical) was a mixture of meta- and para isomers, respectively 60 and 40 %. The product was washed by aqueous HCl and dried. Residual VBC was eliminated by passing on a silica column with ethanol as eluent.

The present work involved investigation of the compound where $n = 2$, with 3 oxygen, further referred to as VEO3.

- Polymerization : polymerizations were carried out at 60°C in degased toluene, passed through an alumina column, as a solvent, under nitrogen atmosphere with AIBN as an initiator ($10^{-2}\text{ mol.l}^{-1}$). Reaction times in all experiments were approximately 20 hrs. For all various feed compositions, the total weight of monomers was maintained constant ($\approx 20\%$, i.e. $1,1\text{ mol.l}^{-1}$). Each monomer was homopolymerized and all experiments were duplicated. Polymers were recovered by precipitation in petroleum ether, filtered, washed and then dried under vacuum at 50°C .
- Analyses : polymerizations were monitored by sampling the reaction mixture at appropriate intervals throughout. Samples were diluted to 1 % weight in THF in the presence of hydroquinone and stored at -10°C . The chromatograph was composed of a Spectraphysics pump, Valco valves, two one-line detectors : a differential Waters R 401 refractometer and a Pye Unicam LC3 UV spectrometer at variable wavelength. Two systems of three Micro-styragel columns ($300 \times 7,8\text{ mm}$) of $100-100-10^4\text{ \AA}$ pore sizes and $500-10^3-10^6\text{ \AA}$ pore sizes were used for elutions with THF of reaction mixture and polymer. The flow-rate was about $0,7\text{ ml.min}^{-1}$.

Complementary analyses of BA were made by gas chromatography with n-decane as an internal standard on a Carbowax 20M column (10 % on chromosorb WAP 80/100 - $2\text{ m} \times 2\text{ mm}$) at 90°C , with an Intersmat IGC 112 F chromatograph. Under these conditions, VEO3 is not vaporized to the column in the injection chamber.

METHODS

With the detectors used for this study, the signal is dependent on the characteristics of the compounds (molar UV absorption ϵ and difference in refractometric indices Δn_x between solvent and solute x), the concentration and analytical conditions : flow-rate, number and concentration of compounds, elution volume ; all these parameters were studied in details ⁴⁾. Concentration is represented by the weight fraction f_x which is the determining parameter, so we may write that surface area of each peak S_x is proportional to f_x and Δn_x : $S_x \propto \Delta n_x \cdot f_x$ where :

$$f_x = \frac{(x)}{\sum(x)}$$

Since the total weight of monomers, polymer and solvent remains constant, $S_x \propto \Delta n_x(x)$ (1).

Each signal is characterized by height h , width w , area S and elution volume V_e at the peak minimum. S is measured with a planimeter or by digital summation⁵). To circumvent changes in dilution and injected volume, each S_x area is divided by that of toluene S_T , used as an internal standard. The ratios of S_M/S_T and S_P/S_T values are determined by linear regression.

In another approach, effect of toluene (present at a higher concentration) is eliminated by considering the S_M/S_P ratio of monomer to polymer peak surface areas.

For a homopolymerization, the monomer consumption obeys first order kinetics $-d(M)/dt = k(M)$, where k includes initiation, propagation, termination rate constants, initiator concentration and efficiency. It may be written $\ln(M)/(M)_0 = -kt = \ln(1-c)/2$ with $c =$ conversion. For low conversion, $c \approx kt$ and polymer $(P) \approx (M)_0 kt$ (3). The S_M/S_P ratio is equal to :

$$\frac{(M)_0 \exp(-kt)}{(M)_0 (1 - \exp(-kt))} \approx \frac{1 - kt}{kt} \quad (4)$$

The corresponding graph $S_M/S_P - 1$ is an hyperbol which fit with experimental points is better if t is corrected by τ , induction time, and a factor V which allows to reach total conversion in a finite time. The form which is used is :

$$u = \frac{\Gamma}{t - \tau} - V \quad (5)$$

where Γ has a time dimension, and decreases as polymerization rate increases. The three parameters t , V , Γ are obtained from a linear form of equation $u(t)$ and linear regression.

The third approach is to consider the balance of the reaction : consumed monomer (s) equal to formed polymer : $|(\Sigma)d(M)/dt| = d(P)/dt$. Then the peaks will correspond to equation :

$$\frac{dS_M}{dt} \cdot \frac{\Delta n_P}{\Delta n_M} = \frac{dS_P}{dt} \quad (6)$$

The above equations may be applied to copolymerization of M_1 and M_2 since the same kinetic laws are obeyed. The difference is in the increase of number and complexity of equations (several rate constants k_p, k_t and refractive indices). For copolymerization, equation (6) is thus

$$\frac{dS_{M1}}{dt} \cdot \frac{\Delta n_{P1}}{\Delta n_{M1}} + \frac{dS_{M2}}{dt} \cdot \frac{\Delta n_{P2}}{\Delta n_{M2}} = \frac{dS_P}{dt} \quad (7)$$

where quantities Δn are obtained from literature data, computation with Lorentz-Lorentz equation, experimental determinations in homopolymerizations and comparison of known and unknown compounds in calibration analyses.

Equation (4) becomes $\Sigma S_{M_i}/S_P \approx (a - bt)/bt$ and is treated in the same way as in homopolymerization.

RESULTS AND DISCUSSION

In the present work, refraction signals were considered mainly. The linearity of signals given by detectors and recorders were verified for a wide range of sensitivities. The analytical system allows a satisfactory separation of components according to their molar weight (fig. 1). Unfortunately, the refractive index of BA is close to that of THF, which leads to a small peak, which is interfered by the large one of toluene (high Δn and large amount), then the values of S_{BA} may have large inaccuracies.

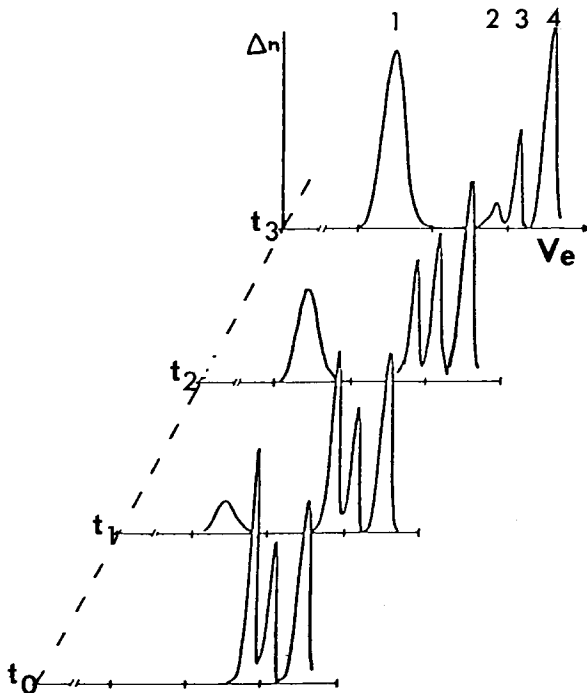


Fig. 1 - Refractometric chromatograms at different conversions

- 1 : copolymer
- 2 : VEO3
- 3 : BA
- 4 : toluene T (sensitivity 1/16 for T)

The evolution of peak surface areas of monomers and copolymers as a function of reaction time is illustrated in fig. 2. Generally, the copolymer curve $P(t)$ is more regular than those of monomers since there is no overlap and side effects of impurities which are encountered at the highest elution volumes. Due to low values of total rate constants k and conversion ratio (except for BA homopolymerizations, where exponential forms are obtained) linear curves are observed.

Some examples of hyperbols $u(t)$ are given on fig. 3 corresponding to various monomer feed. The lower Γ factor, the higher the copolymerization rate when f_{BA} is increased.

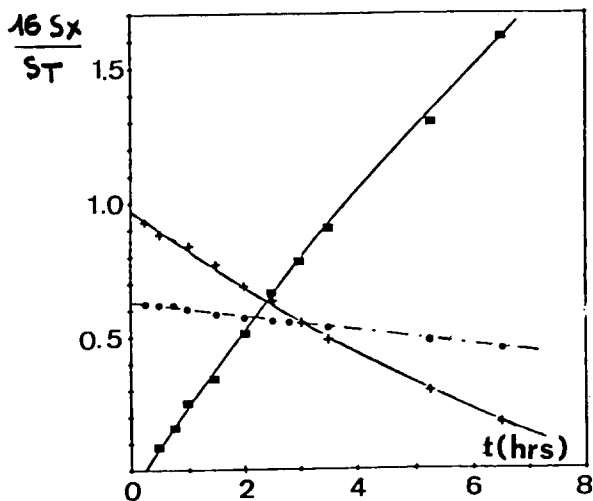


Fig. 2 - Concentration curves of VEO3(+), BA(●) and copolymer (■) from refractometric chromatograms at different times

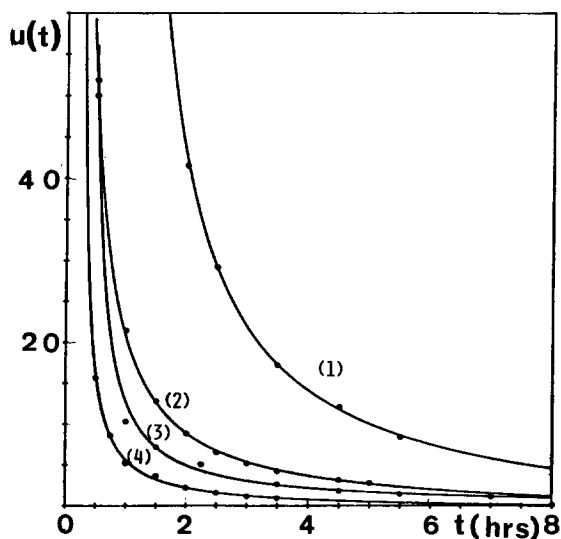


Fig. 3 - Function $u(t)$ for different feed compositions

| | 1 | 2 | 3 | 4 |
|----------|------|------|------|------|
| f_{BA} | 0 | 0.65 | 0.71 | 0.90 |
| Γ | 55.2 | 18.7 | 8.4 | 4.8 |
| τ | 0.8 | 0.14 | 0.34 | 0.21 |

Knowledge of initial values of (M_i) and determination of initial values of slopes of their consumption $d(M_i)$ allow the calculation of r_i through the copolymerization equation in one of its form with instantaneous values and assuming the validity of the terminal model. Three methods were used, according to the equation of :

- Finemann-Ross ⁶⁾ $\frac{n-1}{x} = r_1 \frac{n}{x^2} r_2$ (F.R.)

- Lewis-Mayo ⁷⁾ $r_2 = x \left(\frac{1}{n} (1+r_1 x) - 1 \right)$ (L.M.)

- Kelen-Tüdös ⁸⁾ $\eta = \left(r_1 + \frac{r_2}{\alpha} \right) \xi - \frac{r_2}{\alpha}$ (K.T.)

with $n = d(\text{VEO3})/d(\text{BA})$ $n = (\text{VEO3})/(\text{BA})$

$F = x^2/n$ $G = (n-1)x/n$ $\alpha = (F_{\max} \cdot F_{\min})^{1/2}$ $\eta = G/\alpha + F$ $\xi = F/\alpha + F$

Solved by the least-squares method, the corresponding values are :

| | | | |
|------|--------------|--------------|---|
| F.R. | $r_1 = 2.15$ | $r_2 = 0.27$ | |
| L.M. | $r_1 = 1.6$ | $r_2 = 0.22$ | (extreme values : 1.2 and 2.2 for r_1 |
| K.T. | $r_1 = 1.43$ | $r_2 = 0.21$ | 0.12 and 0.28 for r_2) |

with a confidence 0.3 on r_1 and 0.03 on r_2 .

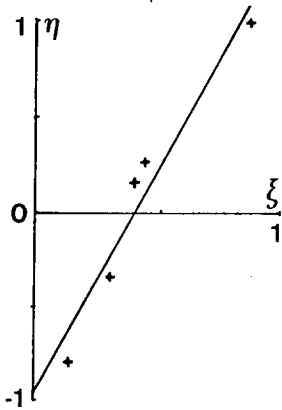


Fig. 4 - Kelen Tüdös treatment as an example of accuracy of the methods for r determination

Effect of these different r values on F_i (molar fraction of i in the copolymer) is represented on fig. 5 by calculation using f_i and r_i in the equation :

$$F_1 = (r_1 f_1^2 + f_1 f_2) / (r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2)$$

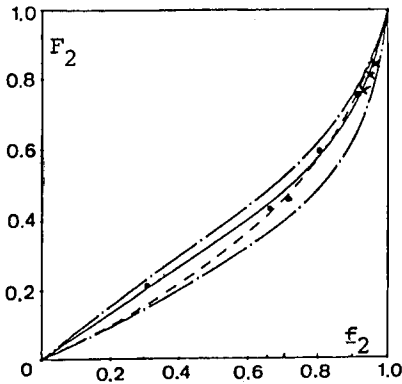


Fig. 5 - Instantaneous copolymer composition vs feed composition for different r values :

K.T. — ; F.R. ----
L.M. —.—

experimental values (●)
one experiment values (x)

From fig. 5, it may be concluded that, without using all possible methods 9, 10), the best agreement is found between experiment values and calculated curves from the K.T. interpretation. It is important to note that relatively large changes in r have no appreciable effect on the curves, and that determining results are those obtained at low BA content.

By using successive values of f and F in one copolymerization at different conversions, agreement was found with the previous set of r values.

By applying equation (6) to homopolymerizations, the $\Delta n_p/\Delta n_M$ ratio is obtained. Under present conditions, values are 4.31. for BA and 1.021 for VEO3, a value which is surprisingly low. The refractive index of VEO3 is close to that of toluene ($n = 1.5$, $d = 1.03$). By using equation(7) the slopes of curves $M_1(t)$ and $P(t)$ (fig. 2) may be compared.

| f_{BA} | 0.00 | 0.65 | 0.71 | 0.80 | 0.90 | 1.00 |
|-----------------|---------|---------|---------|---------|---------|---------|
| ds_{VEO3}/dt | -0.0796 | -0.1615 | -0.1340 | -0.2250 | -0.1375 | |
| ds_{BA}/dt | | -0.0148 | -0.0097 | -0.025 | -0.0300 | -0.4250 |
| ds_p/dt (exp) | 0.0813 | 0.2270 | 0.2167 | 0.3100 | 0.2750 | 1.8310 |
| ds_p/dt (eqn) | 0.0813 | 0.2280 | 0.1780 | 0.3370 | 0.2690 | 1.8310 |

In general, a good agreement between experimental and calculated values are obtained, one exception being for $f_{BA} = 0.71$, where scattering of experimental values does not lead to an accurate value of slope and a precise graph for $u(t)$ (fig. 3).

It may be concluded that size exclusion liquid chromatography is a rapid and useful technique in the determination of copolymerization reactivity ratios. Accuracies are comparable to those of other analytical techniques used to monitor copolymerizations ; an added advantage is the possibility of controlling the balance of monomer(s) and (co)polymer concentrations.

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