# Anomalous Copolymerization Behavior of Styrene and Ethyl Methacrylate at High Conversion

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SUMMARY

    Styrene and ethylmethacrylate were copolymerized in bulk at 62°C and several monomer feed ratios. At moderately high conversion, anomalous copolymerization behaviour occurred. Although the onset of the departures from expected copolymerization behaviour seems to be related to the onset of the gel-effect, this relation did not hold when mimicking higher conversion by adding an amount of homopolymer.
    Obviously the propagation reactions are not only affected by changes in diffusion characteristics but also by changes in other medium characteristics e.g. interactions between monomeric and copolymeric species.

INTRODUCTION
    In many cases the course of a copolymerization process can be described by models considering both monomer reactivity and ultimate unit dependent chain-end reactivity. Among these models, the well-known classical Alfrey-Mayo (AM) model is outstanding. From many studies on copolymers, however, the r-values appear to be dependent on the nature of the solvent (1-5) pressure (3) and temperature (6) but assumingly independent of conversion provided the degree of conversion is moderate and the system is diluted.
    However, from recent reviews it becomes clear that in some cases even the integrated Alfrey-Mayo model is inadequate to describe the copolymerization behaviour up to high conversions. For example, Johnson (7) and Dionisio (8) reported anomalous behaviour in the copolymerization of the system styrene methyl methacrylate, Kelen (9) in the copolymerization of vinylidene cyanide-maleic anhydride and Zil'Berman (10) in the copolymerization of methacrylamide-methacrylic acid.
    Recently, we have studied the system styrene-ethyl methacrylate in bulk. We found experimental curves of monomer feed ratio versus conversion that deviate significantly from the relationships to be expected on the grounds of the integrated AM model. Both monomer feed ratio (q) and conversion were calculated from data obtained by quantitatively monitoring monomer concentrations by means of GLC during the entire course of the reaction. This method, introduced by German and Heikens (11, 12), is particularly useful in studies on high

conversion copolymerization since the course of the process can be detected in detail and very easily. In addition, copolymer compositional analysis becomes redundant, thus avoiding all pertaining errors (e.g. fractionation according to composition during the working-up procedure).

In contradiction to the explanation given until now by other investigators for similar phenomena concerning other systems, our results unambiguously indicate that the departures from the Alfrey-Mayo model occur before the onset of the gel effect. Here we define the onset of the gel effect as the moment at which a significant increase in conversion rate occurs.

These novel findings are described in the present paper and will be the subject of further investigation.

EXPERIMENTAL

The monomers styrene and ethyl methacrylate were distilled at reduced pressure under nitrogen. The middle fraction of the distillate was collected and used. In all cases the distillate was found to be > 99.5% pure by GLC analysis. The free radical initiator AIBN (Fluka p.a.) was used without further purification. The initiator concentration was 40 mmol/l.

All bulk copolymerizations were carried out in a stainless steel S.F.S. reactor which was flushed with nitrogen before use. The reaction mixtures were thermostated at 62°C ± 0.2°C and stirred at 100 rpm. The reaction mixture was sampled at predetermined time intervals. The samples were kept in a cooled beaker and then dissolved in THF which also served as the internal standard. Two microliter of each sample were injected at least twice. The GLC conditions were: stationary phase, 10-15% by wt of squalance on chromosorb W AW DMCS 80 - 100 mesh (Johns Manville); column length 2.5 meter and column temperature 371 K, detector temperature 420 K and injection port temperature 393 K.

Density measurements have been carried out by means of a vibration tube densimeter (Paar Precision Density Meter, Model DMA 10).

Viscosity data were obtained by means of a cone and plate viscosimeter (Rotavisco). Both density and viscosity were determined at reaction temperature i.e. 62°C.

RESULTS AND DISCUSSION

The r-values of the system styrene (sty) and ethyl methacrylate (ema) have been evaluated by means of the improved curve fitting I procedure (1, 13). Only low conversion data were taken into account. The results are summarized in table I.

Table I    Reactivity ratios of sty (1) and ema (2) in different media, at 62°C.

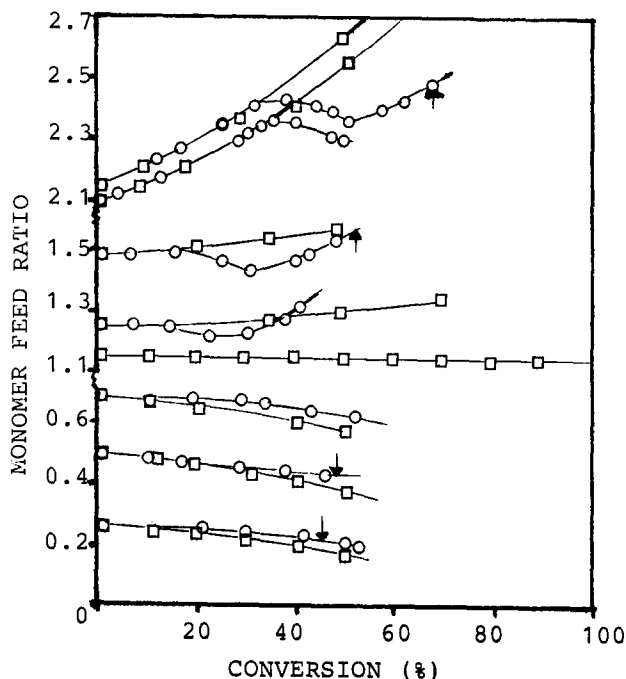| medium | r1 | r2 |
|--------|-----|-----|
| bulk | 0.46 ± 0.03 | 0.38 ± 0.04 |
| toluene | 0.49 ± 0.02 | 0.40 ± 0.03 |

Fig. 1
(O) observed and
(□) predicted re-
lation between
conversion and mo-
nomer feed ratio.

If the integrated AM model is valid at any conversion, the relations of monomer feed ratio versus conversion can be predicted by means of r-values determined at low conversions and using the integrated AM equation according to (1):

$$f_t = \{1 - [(q/q_0)^{-x_2+1} \times (\frac{x_2 q - x_1}{x_2 q_0 - x_1})^{x_1+x_2+1} \times (\frac{q+1}{q_0+1})]\} \times 100\% \quad (1)$$

where $f_t = (1 - [M]/[M]_0)\ 100\%$ is the total conversion of monomer, $[M] = [M_1] + [M_2]$, $M_1$ is monomer (i), o indicates initial conditions, $q = [M_1]/[M_2]$ represents the monomer feed ratio, $x_1 = (r_1 - 1)^{-1}$ and $x_2 = (r_2 - 1)^{-1}$.

The observed and predicted relation of monomer feed ratio versus conversion are represented in figure 1. From this figure it becomes obvious that the extent and the starting point of anomalous copolymerization behaviour strongly depends on the initial monomer feed ratio ($q_0$). Copolymerizations with initial monomer feed ratios $q > q$ azeotrope ($q_{az}$) are showing a considerable decrease of q, starting at high conversions. On the other hand, reactions with initial monomer feed ratios $q < q_{az}$ are showing smaller departures from the predicted relation, starting at lower conversions. The arrows in the figure indicate the point of conversion at which the gel-effect becomes operative.
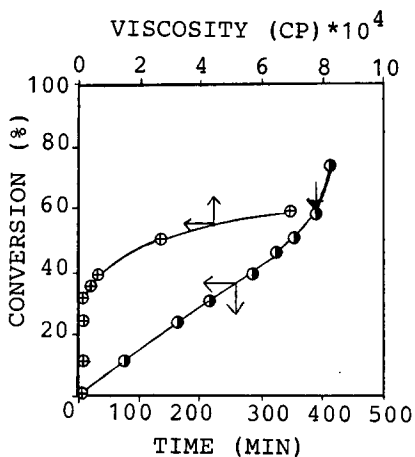
VISCOSITY (CP) *10$^4$



Fig. 2 Observed relations between (◐) conversion-time and (⊕) conversion-viscosity $q_0 = 2.51$
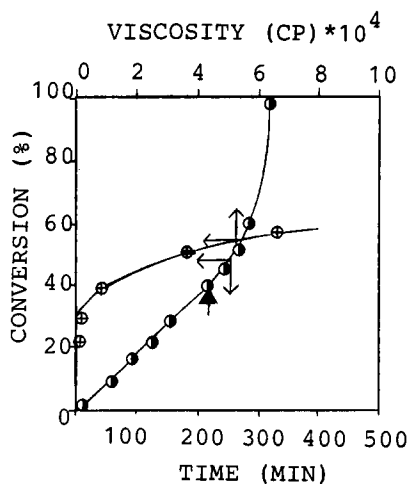
VISCOSITY (CP) *10$^4$



Fig. 3 Observed relations between (◐) conversion-time and (⊕) conversion viscosity $q_0 = 0.52$
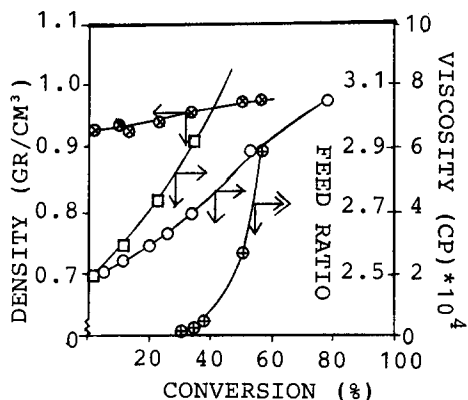


Fig. 4 Relations between (⊗) density, (⊕) viscosity, (O) observed and (□) theoretical q and conversion. $q_0 = 2.51$
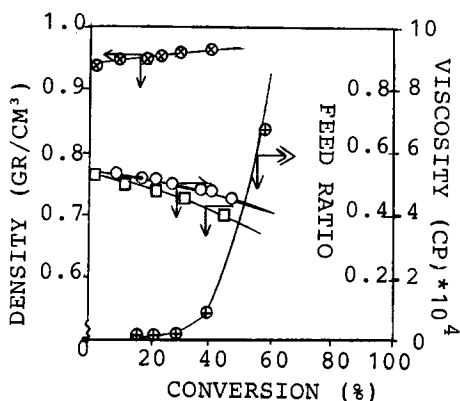


Fig. 5 Relations between (⊗) density, (⊕) viscosity, (O) observed and (□) theoretical q and conversion. $q_0 = 0.52$

Until now deviations of this type have been attributed to the occurrence of gellation, at least locally, as may be the case in precipitation (co)polymerization. Furthermore, it is assumed that at the onset of the gel-effect not only termination but also chain propagation becomes diffusion controlled.

If the diffusion rates of both monomers are not equally affected, this would result in apparent r-values.

However, during our experiments no precipitation of polymer or any turbidity were observed during the course of the reaction, ruling out the possibility of heterogeneity as an explanation for the observed phenomena.

Although the start of the anomalous copolymerization behaviour seems to be shifting with the start of the gel-effect, it becomes apparent that the observed departures are occurring long before the onset of the gel-effect. The question rises whether the viscosity or the changing reaction medium (decreasing polarity, changing preferential solvation etc.) causes the departures from expected reaction kinetics.

From figure 1 it appears that the distance between the onset of the gel-effect and the conversion at which the anomalous copolymerization behaviour starts is nearly constant and approximate 35% conversion. These results indicate that propagation constants can be affected well in advance of the gel-effect.

In a first attempt to shed some light on the phenomena, we carried out two additional experiments. One with an initial feed ratio $q_0 = 2.51$ and one with $q_0 = 0.52$, after adding poly(ethyl methacrylate) (10 wt%, $M_n = 49.000$). The results are given in figures 2 through 5.

As a first approximation, the onset of the gel-effect, i.e. the conversion at which a sudden increase in conversion rate occurs would be expected to show up roughly 10% earlier in conversion as compared with copolymerizations without initial addition of homopolymer. This behaviour is indeed observed since the gel point of the copolymerization with $q_0 = 2.51$ (figures 2 and 4) shifts from 73% (see fig. 1) to 60% conversion and the gel point of the copolymerization with $q_0 = 0.52$ (figures 3 and 5) shifts from 48% to 39% conversion.

However, the point of conversion at which the anomalous behaviour occurs, shifts from 39% to 0% in case of $q_0 = 2.51$ and from 20% to 0% in case of $q_0 = 0.52$, when homopolymer is present. If only viscosity would cause the anomalous behaviour, the distance between the onset of the gel-effect and the starting point of the anomalous copolymerization would be expected to remain about 35% as in fig. 1, despite the presence of homopolymer.

Moreover, the curves of the observed q-conversion relation might be expected to maintain their shapes if the added homopolymer would only act as an inert thickener that only mimics a higher conversion. In case of $q_0 = 0.51$ the shape changes somewhat, but not significantly as compared with figure 1. In case of $q_0 = 2.51$, the shape changes dramatically.

These observations clearly indicate that viscosity is nct
the only factor in the present anomalous copolymerization be-
haviour. The changing reaction medium seems to have an important
influence on the observed anomalous kinetics. Effects of
changing interactions between monomers (in our experiments
also solvent) and (co)polymer will have to be taken into
account. For instance, decreasing medium polarity with increasing
conversion or changing preferential chain solvation or immi-
scibility among copolymer species of different composition
produced at different stages of reaction (14) may play an
important role.

Although the complete explanation of the nature of the
present anomalous copolymerization behaviour at high conver-
sions can not be presented yet, the results certainly indicate
an interesting line of development that needs a considerably
broader experimental basis as well as an extended theoretical
treatment. The phenomena will be studied in further detail
in our laboratory.

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