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Polymerization of acrylamide in solution and inverse emulsion: number molecular weight distribution with chain transfer agent

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Abstract

The molecular weight distributions of the free-radical polymerization of acrylamide in solution and in inverse emulsion are examined as a function of concentrations of initiator and of amount of added chain transfer agent (sodium formate). When these distributions are displayed as ln(number molecular weight distribution), readily obtained from the GPC trace (essentially by dividing by the square of molecular weight), the results can be semi-quantitatively interpreted in terms of the amounts of chain stoppage by transfer and by termination.

Keywords: Molecular weight distribution; Inverse emulsion; Polymerization of acrylamide

1. Introduction

It has been shown that the shape of the number molecular weight distribution (MWD) can be used to study mechanisms involved in free-radical polymerizations, and also to obtain values of transfer and termination rate coefficients [1–10]. The number MWD, $P(M)$, which is the number of chains with molecular weight M, contains the same information that is present in the GPC distribution (and is trivially obtained from the GPC trace, as discussed later, in the simplest case merely by dividing the GPC signal by M^2); detailed considerations of the mechanisms of free-radical polymerization show that qualitative and quantitative elucidation of these mechanisms can be obtained from the appearance of ln $P(M)$ as a function of M. Molecular weight distributions obtained from an experimental sample are always *cumulative* distributions, but mechanistic information is best obtained from *instantaneous* MWDs. These can be obtained (at least in principle) by taking samples at successive conversions and subtracting the appropriately-normalized distributions.

This note deals with the first examination of the number molecular weight distribution of a water-soluble polymer (polyacrylamide) polymerized in solution and in inverse emulsion (water in oil) polymerization. We study the shape of this number distribution as a function of the amount of chain transfer agent (sodium formate) and of initiator. Sodium formate is a chain transfer agent commonly used in inverse emulsion polymerization [11]. Potassium persulfate (KPS) and 2,2′-azobisisobutyronitrile (AIBN) were used as initiator in solution and in inverse emulsion polymerization, respectively.

In a water-in-oil polymerization, a hydrophillic monomer (usually in aqueous solution) is dispersed in a continuous organic phase using a water-in-oil emulsifier. The free-radical polymerization is carried out to yield an inverse latex, i.e. a colloidal dispersion of water swollen polymer particles in oil. Such a process is well suited to the preparation of high molar mass polymers at rapid reaction rates [12,13], due to the high local monomer concentration within the particles and to the fact that free radicals grow in separate particles, which if the average number of radicals per particle is sufficiently low may prevent their mutual termination. If these polymers contain anionic or cationic charges, they are effective flocculants for many substances, including sewage, cellulosic fibres and fines for retention in paper-making, coal tailings and in general applications whenever aqueous–solid separations are required [14]. For such applications, the polymer must have a molecular weight as high as possible, because one of the contributing mechanisms for flocculation is bridging between solid particles [15,16]. Mechanistic understanding in inverse

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Table 1
Recipes for solution polymerization of acrylamide (Am)

	S	S: 2I	S: A/3
Acrylamide (wt%)	3.03	3.03	3.01
Water (wt%)	89.83	85.87	91.92
5 wt% aqueous solution of HCOONa (wt%)	3.14	3.11	1.07
0.3 wt% aqueous solution of KPS (wt%)	4.00	7.99	4.00
[HCOONa]/[Am] (%)	5.40	5.40	1.89
[KPS]/[Am] (%)	0.10	0.21	0.10

emulsion polymerizations, therefore, can provide guidance for synthesis of polymers with high molecular weight.

2. Experimental

Acrylamide (AM) from Cytec was recrystallized twice from chloroform (m.p. = 84°C). The purity of formic acid (Jansen Chem.) was measured by pHmetry: an aqueous solution of formic acid was added to a solution of sodium hydroxide until the equivalence point. All water was deionized (Millipore). Potassium persulfate (KPS, Aldrich) and AIBN (DuPont), were used as received.

For inverse emulsion polymerizations, the oil was a narrow cut isoparaffinic mixture, LVT 200 from Conoco, used as supplied. The emulsifier (Hypermer 2524, ICI) is a polymeric surfactant which also contains some sorbitan monooleate, and was used as received. Sodium ethylene diamine tetraacetic acid (EDTA(Na)) from ICI was used as a chelating agent, to eliminate catalysis of persulfate decomposition by traces of transition metal ions.

Polyacrylamide samples were prepared as follows:

1. Solution polymerizations (Table 1) were carried out in a glass reactor. The starting recipe (without the KPS solution) was first purged with purified N_2 to remove most residual oxygen. The temperature was maintained at $50 \pm 0.1°C$. The initiator solution was injected after thermal equilibration.
2. Emulsion polymerizations (Table 2) were carried out in a glass reactor. The aqueous phase and oil phases were prepared separately. The aqueous phase was then poured into the oil phase under strong shear with an Ultra-Turax. The emulsion was injected into the reactor and purged with purified N_2. The agitation rate was fixed at 280 rpm and temperature was maintained at 50 ± 3°C. AIBN solution was then injected.

Table 2
Recipes for polymerization of acrylamide in inverse emulsion

	E	E:2I	E:A/3
Acrylamide (wt%)	25.37	25.08	25.23
Water (wt%)	38.19	38.38	39.25
HCOONa (wt%)	1.26	1.32	0.44
CH_3COONa (wt%)	5.26	5.03	5.00
EDTA(Na) (wt%)	0.10	0.10	0.10
LVT 200 (wt%)	27.82	28.07	27.97
Hypermer 2524 (wt%)	1.99	2.02	2.00
AIBN (wt%)	0.0176	0.0319	0.0132
[HCOONA]/[AM] (%)	5.19	5.50	1.82
[AIBN]/[AM] (%)	0.0029	0.0055	0.0023

For each procedure (solution and emulsion polymerization), three experiments were performed: a reference one, one where the concentration of initiator was doubled ('2I') and one where the concentration in transfer agent was divided by three ('A/3').

Solution polymerizations were stopped after 13–18 min; two aliquots were withdrawn during emulsion polymerizations. For both solution and emulsion polymerizations, polyacrylamide was recovered from the reaction medium by precipitation in excess methanol containing a small amount of hydroquinone, followed by several washings and drying at 45°C.

GPC analysis was carried out with a Waters GPC (Model 5000) with an Erma dRI Model ERC 7500 detector. The mobile phase was water with sodium nitrate (0.25 M) and sodium hydrogenphosphate (0.01 M). Two columns, a Shodex model KB-806 and a Waters hydrogel linear (part number 11-545) with a length of 33 cm each, were used. Calibration was with narrow-distribution polyethylene oxide (PEO) standards (six standards covering the molecular weight range from 2.1×10^4 to 9.63×10^5). With the aqueous GPC set-up used here, molecular weights exceeding 2×10^6 have no significance because such chains are totally excluded from the columns.

The number molecular weight distribution is obtained from the GPC trace as follows [2,17]. Assume for the moment that the GPC calibration curve relating elution volume V to molecular weight is linear: $V = a \log_{10} M + b$. The GPC trace is then also the cumulative GPC distribution, $w(\log_{10} M)$, and this is related to the cumulative number MWD $\bar{P}(M)$ by:

$$\bar{P}(M) = \frac{w(\log_{10} M)}{M^2} \tag{1}$$

Extensions of this expression to the more common case where the calibration curve is non-linear have been given elsewhere [2,17]; note that certain GPC analysis packages automatically correct for nonlinearity and produce $w(\log_{10} M)$ directly. The number- and weight-average molecular weights, $< M_n >$ and $< M_w >$, are respectively the ratio of the first to the zero-th, and the second to the first, moments of $\bar{P}(M)$. As stated, in principle the instantaneous

Table 3
Conversion, weight-average molecular weight, number-average molecular weight and polydispersity index for samples recovered from solution and emulsion polymerization reactive medium. Molecular weights are relative to PEO

	S	S:2I	S:A/3	E		E:2I		E:A/3	
Conversion (%)	20.6	21.7	19.2	27.4	46.3	58.4	64.9	24.4	54.3
$< M_w > /10^5$	5.6	6.9	12.7	3.0	3.3	2.0	3.2	8.2	7.8
$< M_n > /10^5$	2.3	2.0	4.5	0.9	1.2	0.9	1.1	3.2	2.2
γ	2.5	3.4	2.9	3.2	2.9	2.2	3.1	2.6	3.6

number MWD $P(M)$ can be obtained by subtraction of successive, appropriately-normalized, $\bar{P}(M)$ [18]. The reason for the use of $P(M)$ is that theory [2,6] shows that, in a system such as an inverse microemulsion of acrylamide, where the particles are large and hence in which the system follows pseudo-bulk [1] kinetics, one has:

$$M \xrightarrow{\lim} \infty P(M) = (\text{normalization constant})) \times \exp\left\{ \frac{k_{tr,M} C_P + k_{tr,A} C_A + (< k_t > \bar{n}/N_A V_s)}{k_p C_P} \frac{M}{M_0} \right\} \quad (2)$$

where k_p, $k_{tr,M}$ and $k_{tr,A}$ are respectively the rate coefficients for propagation and transfer to monomer and to chain transfer agent, M_0 is the molecular weight of monomer, C_P and C_A are the concentrations of monomer and chain transfer agent inside the particles, $\bar{n}$ is the average number of radicals per particle, N_A is Avogadro's constant, $< k_t >$ is the average of the (chain-length-dependent) termination rate coefficient over the radical length distribution in the system, and V_s is the swollen volume of the particles. This result is based on the realization that the dominant mode of termination in a pseudo-bulk system is between a long and a short radical; the same expression holds for a solution or bulk polymerization, except that the term in $\bar{n}$ is replaced by a corresponding factor with the radical concentration. Eq. (2) shows that a linear ln $P(M)$ is expected for higher molecular weights; simulations [2] suggest that this linearity is expected to hold down to quite low values of M, typically for $M > 10^4$. It is therefore convenient to examine data in the form of the slope L of a ln $P(M)$ plot:

$$\Lambda(M) = \frac{\mathrm{d} \ln P(M)}{\mathrm{d}M} \quad (3)$$

For example, in a transfer-dominated system, $L = (k_{tr}/k_p) M_0^{-1}$, while the deviations of L from a constant value for a true instantaneous MWD suggest the presence of unexpected mechanisms [6]. Eq. (2) also implies that the *cumulative* number distribution should show concave-up behaviour if the system is either dominated: (a) by transfer to chain-transfer agent which is consumed during the course of the polymerization [1], and/or (b) by termination, as the polymerization rate decreases (e.g., Ref. [7]) and longer chains are formed.

According to Eq. (2), by using different initial concentrations of transfer agent and of initiator, it is possible to know which reaction dominates chain-stopping in the system: transfer to chain transfer agent or to monomer, termination between two growing radicals, and/or to indicate if other reactions or processes have to be considered.

In looking at ln $P(M)$ curves, it is important to concentrate on those regions where most polymer is formed (especially the value of M between the peak molecular weight and $< M_w >$ [4–6]; data at higher molecular weights often are prone to error, as only a tiny amount of polymer is involved and thus the $P(M)$ is very sensitive to baseline subtraction. However, it is also noted that the small amount of polymer formed at these very high molecular weights often may have a large effect on polymer properties (e.g., as noted, these long chains can be very effective in flocculation). While these regions are certainly worthy of further study, this is not attempted here because of the experimental difficulties.

3. Results and conclusions

Conversions at which samples were recovered from solution and emulsion polymerization are given in Table 3, as are the weight- and number-average molecular weights, and the polydispersity index γ, obtained from GPC.

From the $< M_w >$ values given in Table 3, it is seen that the molecular weight of samples polymerized in solution are higher than for emulsion polymerization. This result might be seen as surprising, since it is often believed that polymerization in dispersed media gives higher molecular weights than in homogeneous media, because of compartmentalization (isolation of radicals in separate particles). However, it is quite common for emulsion polymerizations, especially ones involving particles as large as are found in inverse emulsion polymerizations, to follow pseudo-bulk kinetics [1], when molecular weights will be governed by considerations similar to those in bulk, and hence where overall radical flux (initiator concentration) rather than any compartmentalization effects dominate the molecular weight.

Figs. 1 and 3 give the GPC distributions, and Figs. 2 and 4 the cumulative number molecular weight distributions of samples polymerized in solution and emulsion. Fig. 4 also

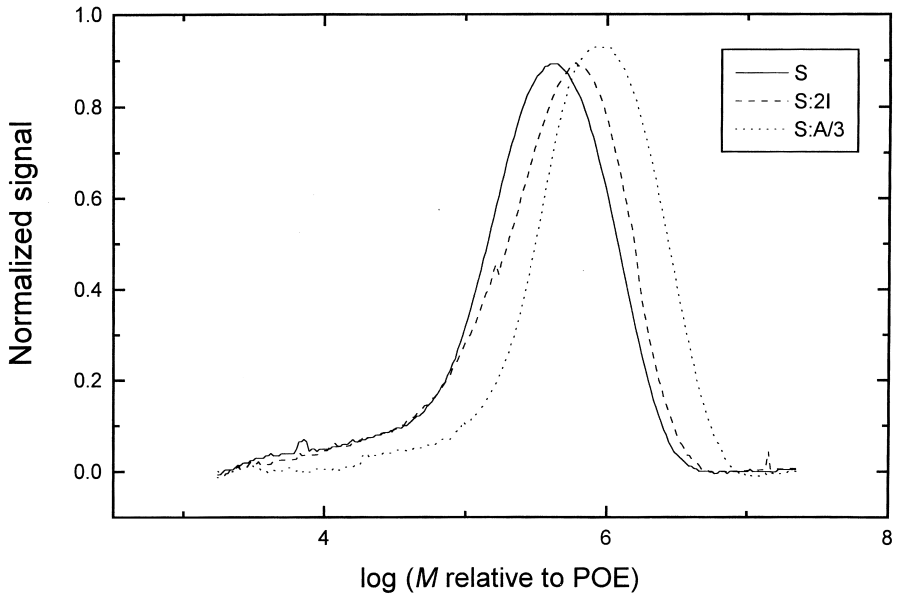

Fig. 1. GPC distributions for solution polymerization.

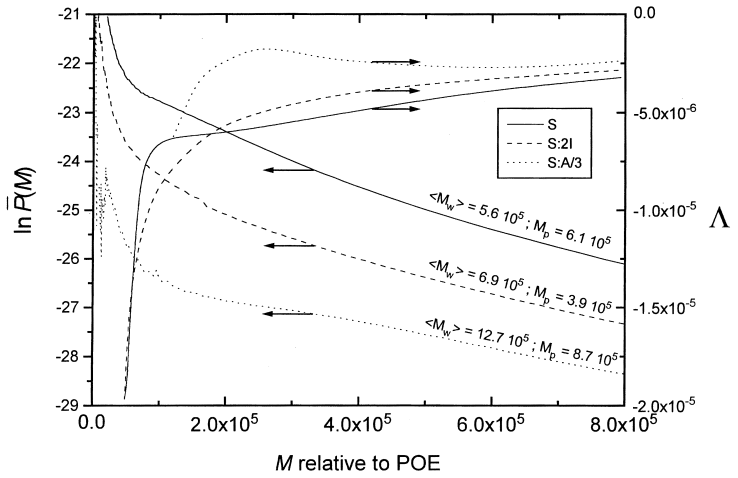

Fig. 2. ln $\bar{P}(M)$ (left-hand axis) and slope L (right-hand axis) for solution polymerization, with $< M_w >$ and M_p (peak molecular weight from GPC) marked on each line.

gives the 'pseudo-instantaneous' number MWD, obtained by subtraction and being for polymer chains created between the two conversions given in Table 3.

Fig. 2 shows the expected effect of chain transfer agent: the number distributions show a rapid decay for the high M values; the apparent maximum in ln $\bar{P}(M)$ for one of the runs may or may not be an artifact due to low molecular weight species formed during the induction period, etc. [18]. The shapes of these curves, along with the dependences on initiator and chain transfer agent concentrations, are consistent with chain stoppage by both termination and by transfer to transfer agent. The high amount of low molecular weight polymer chains ($M < 10^5$) can be explained by reactions occurring between 0% conversion and the concentration of polymer where chains overlap (c^*). More detailed interpretation of these data is difficult because they cover a

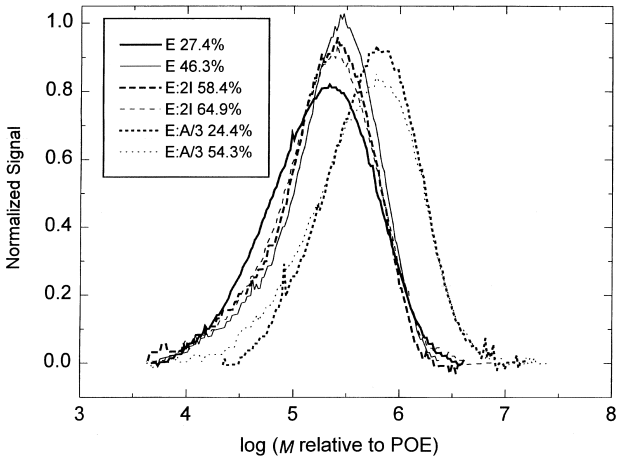

Fig. 3. GPC distributions for inverse emulsion polymerization.

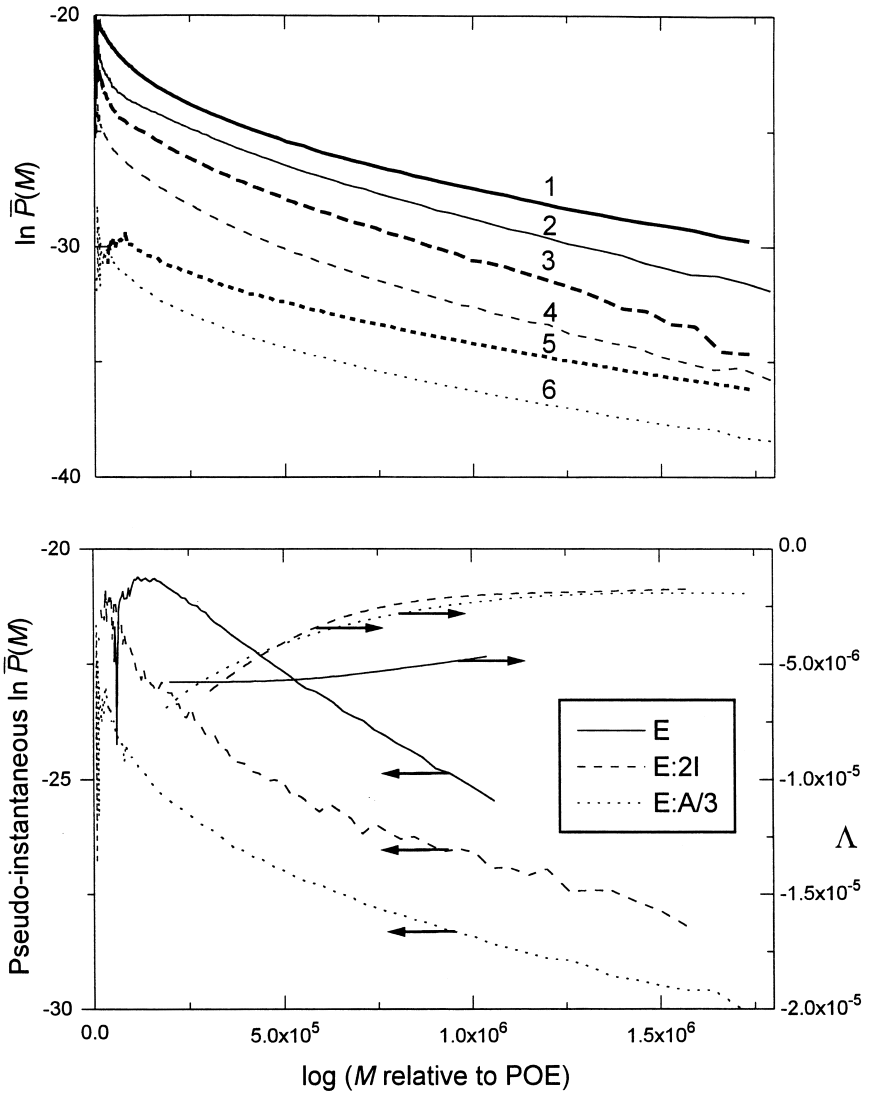

Fig. 4. ln $\bar{P}(M)$ and ln $P(M)$ (pseudo-instantaneous) (left-hand axis) and slope L (right-hand axis) for emulsion, with $< M_w >$ and M_p marked on each line. Key:

Number	Name	Conversion (%)	$< M_w >$	M_p
1	E	27.4	3.0×10^5	2.1×10^5
2	E	46.3	3.3×10^5	2.8×10^5
3	E:2I	58.4	2.0×10^5	2.3×10^5
4	E:2I	64.9	2.3×10^5	2.3×10^5
5	E:A/3	24.2	3.5×10^5	3.5×10^5
6	E:A/3	54.3	7.8×10^5	3.4×10^5

relatively wide range of conversion, including very low conversions where MWDs can be vitiated by, e.g., low molecular weight species formed during the induction period.

For emulsion systems, MWDs are made complex by the events occurring during particle formation [3]. Figs. 3 and 4 show the (cumulative) GPC and ln $\bar{P}(M)$ distributions, and the pseudo-instantaneous distributions corresponding to chains created between 27.4 and 46.3% conversion (E), 58.4 and 65.9% conversion (E:2I) and 24.4 and 54.3% conversion (E:A/3). The pseudo-instantaneous distributions at higher conversions enable the complexities of particle formation (which is in fact droplet nucleation in an inverse emulsion polymerization) to be obviated in the data interpretation. Sample E gives a number MWD which is quite linear for $M > 2 \times 10^5$. This suggests that under these conditions, chain-stoppage is dominated by transfer to chain transfer agent, whose concentration is essentially constant (i.e., its original concentration was sufficiently high that it has not been greatly consumed). While Eq. (2)

suggests that a linear ln $P(M)$ could also be obtained in a system with significant chain-stoppage by termination, the conversion range for this pseudo-instantaneous MWD sample is such that one would expect a significant change in termination rate coefficient over the period in which the sample was obtained, which would give a nonlinear ln $\bar{P}(M)$ (this change arises because termination is diffusion-controlled [19], and diffusion coefficients decrease with increasing polymer fraction). One sees that decreasing the amount of chain transfer agent (E:A/3) results in a more nonlinear ln $P(M)$ and a higher $< M_w >$, consistent with both termination and transfer being chain-stopping events. Increasing the initiator concentration (E:2I) also gives a more nonlinear ln $P(M)$, where the slope at higher M ($> 6 \times 10^5$) is *less* than that for E, which is proposed to be almost entirely transfer-dominated. This at first seems strange, since increasing initiator concentration will increase the amount of termination, which (on top of pre-existing transfer) can only *decrease* the slope, as is seen in Eq. (2). However, the increase in the number of radicals which results from increasing the initiator concentration will also increase the rate at which chain transfer agent is consumed, and thus at higher conversions (when less chain transfer agent is present) this can result in a decreased amount of chain stoppage by transfer, and a thus higher overall molecular weight.

It is noted from Fig. 2 that sample E apparently does not give any low molecular species ($M < 1.5 \times 10^5$), whereas the two other samples seem to contain a high amount of those species. However, it has been established that the subtraction necessary to obtain these pseudo-instantaneous distributions can often lead to artifacts at lower M [6,18]; further investigation is needed to clarify this by taking samples at different concentrations.

In summary, the qualitative effects of chain transfer agent on the full number MWDs can be understood by the procedures used here. Quantification of the MWDs to yield values for $k_{tr,A}$ and $< k_t >$ could be obtained by taking samples over a wider range of conversions, initiator concentrations and concentrations of chain transfer agent [6]; such studies would lead to improved means of controlling MWDs and hence flocculation performance.

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