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Living poly(α -methylstyrene) near the polymerization line.

VII. Molecular weight distribution in a good solvent

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We have measured the molecular weight distribution (MWD) in a case of equilibrium polymerization. We have studied the time development of the MWD of “living” bifunctional poly(α -methylstyrene) in tetrahydrofuran after a quench to 21 K below the polymerization temperature, T_p . We see an intermediate Gaussian distribution evolving toward a final exponential distribution, as expected from theoretical considerations. We see a longer equilibration time for the number average molecular weight (M_n) as well as for the weight average molecular weight (M_w) than for the monomer concentration ($[M]$), whereas theories predict that M_n and $[M]$ will relax together and that M_w will take much longer. We attribute the delayed equilibration and a second peak at about $M_n/4$ to the effects of ionic aggregation of the living polymers. We have also studied the equilibrium MWD of this system as a function of the temperature below T_p , and thus as a function of the number average degree of polymerization (L). These measurements and the time study discussed above are the first experimental evidence that the equilibrium MWD for an organic polymer in a state of equilibrium polymerization is an exponential/Flory–Schulz distribution, and is consistent with scaling predictions. Near T_p and at low L , we observe a deviation from the exponential distribution, which may be evidence of the effect of a chain-length dependence of the equilibrium constant for polymerization, or of the effects of polydispersity on correlations due to excluded volume. In addition, the measured L is about two times less than that expected from the initiator concentration; this could result from ionic aggregation or from chain transfer reactions.

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I. INTRODUCTION AND THEORETICAL BACKGROUND

“Living” polymerizations, in which the polymer remains chemically active, have become a mainstay of polymer synthesis, because (1) they can produce narrow molecular weight distributions, and (2) the living ends permit the synthesis of various polymer architectures.^{1–3} In order to understand living polymerizations, we need to understand the time development of the molecular weight distribution (MWD), from initiation to true equilibrium.

The literature on molecular weight distributions in polymers is vast, including considerations of various reaction mechanisms.^{4,5} We confine our discussion here to a bifunctional anionic polymerization to form a flexible linear polymer in a batch process in a solvent, with two steps.⁶ The first is an initiation step,



k'_i ,

where I , M , ${}^{\sim}M_2^-$ stand for initiator, monomer, and activated dimer with two living ends, respectively, and k_i and k'_i are the forward and reverse rate constants. The initiation step can sometimes be viewed as essentially complete and irreversible, as in the case of interest here, and thus the number of polymer molecules is fixed by the number of initiator molecules. The second step is a reversible propagation step,



or, in general,



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where x is the number of monomers in the polymer (or the degree of polymerization, DP), and k_p and k_d are the rate constants for propagation and depropagation.

This basic mechanism does not include scission, recombination, chain transfer, or termination. The rate constants k_p and k_d can, in principle, depend upon the chain length, in addition to the expected dependence on solvent, initiator, and temperature. In addition, the cationic counterion can be closely associated with the polymeric anion as an ion pair, or less closely associated as a solvent-separated or even free ion.⁷ These different states of the ion pair can have different rate constants that contribute independently to the kinetics.⁸ We will assume that the states of the ion pair interconvert sufficiently rapidly that they need not be considered as independent species.

The issue of the time development of the MWD for a reversible living polymerization was first addressed in 1958 by Brown and Szwarc (BS).⁹ BS studied the kinetic equations, assuming the rate constants to be independent of chain length, and recognized three stages of the MWD development.

A. Stage 1: When $k_p \gg k_d$, the initial MWD is expected to be a narrow, Poisson distribution⁴

In this stage, all initiated sites are equally likely to react, and the initiation and propagation are much faster than the depropagation, so that the polymerization is “temporarily irreversible.” In this case, the number fraction of polymers of size x , n_x , is^{5,10}

$$n_x^P = e^{-(L-1)} L^{x-1} / (x-1)!, \quad (4)$$

where L is the number average degree of polymerization (counting the polymers and initiated monomer, but not the free monomer¹¹) and the superscript “P” denotes the Poisson distribution. The polydispersity index ($PDI = M_w/M_n$, where M_w and M_n are the weight and number average molecular weights) for the Poisson distribution is $[1 + (1/L)]$, which approaches unity only at high degrees of polymerization.

B. Stage 2: The equilibrium concentration of monomer, $[M]$, is attained after the initial Poisson distribution, but long before the final, equilibrium MWD

M_n will be established during this intermediate stage and will remain nearly constant thereafter, while M_w will continue to increase until the equilibrium MWD is established. Thus the relaxation of the enthalpy is completed during this stage, but the relaxation of the entropy is not yet achieved.

C. Stage 3: The final, equilibrium MWD is expected to be a broad Flory–Schulz “most probable” distribution^{5,12,13}

The final equilibrium MWD can be calculated from the kinetic equations,¹⁴ or from statistical arguments,^{15,16} which will yield mean-field predictions. Non-mean-field predictions which take into account correlations due to excluded volume can be calculated from statistical mechanics via scaling and/or renormalization group theory. In the mean-field ap-

proximation, implicit in BS, the Flory–Schulz (FS) number distribution is expected when the depropagation also proceeds and equilibrium is established. For all sites equally likely to react,

$$n_x^{\text{FS}} = p^{x-1} (1-p), \quad (5)$$

where $p = 1 - (1/L)$. The PDI for the Flory–Schulz distribution is $(1+p)$, which becomes 2 at high degrees of polymerization, where L is large and $p \rightarrow 1$. When $p \rightarrow 1$, Eq. (5) becomes⁴

$$n_x^E = (1/L) \exp(-x/L), \quad (6)$$

and thus the Flory–Schulz distribution becomes (and is often called) the “exponential distribution.” The exponential distribution is also predicted from chemical kinetics¹⁷ and from a Flory–Huggins lattice model.¹¹ Szwarc^{7,18} argued that the Flory–Schulz number distribution for a polymer with two active sites differs from that for one active site, and should be:

$$n_x^{\text{SZ}} = (x+1)p^x(1-p)^2, \quad (7)$$

which gives a narrower MWD with a limiting PDI of 1.5. However, others^{11,16,19} argue that the (mean-field) equilibrium MWD is given by Eqs. (5) or (6), regardless of whether the polymer chain is monofunctional or bifunctional.

The equilibrium MWD for this basic mechanism has been addressed often since BS. The assumptions leading to Eqs. (5) and (6) are (i) that the rate constant is independent of degree of polymerization or that the free energy of polymerization is independent of degree of polymerization (“equal reactivity”), (ii) that the solution is ideal, and (iii) that a mean field prevails. These assumptions are neither entirely independent of one another, nor entirely equivalent to one another. Various attempts have been made to calculate the MWD without these assumptions. The issue of nonideality was addressed by Harris,²⁰ who found that a Flory–Huggins¹⁰ treatment of the nonideality gives the same MWD as does as an assumption of ideality, but that a Guggenheim²¹ treatment of the nonideality broadens the MWD significantly, especially at high concentrations. Lundberg²² later argued that the final MWD depends on whether the entropy of polymerization of a pure homopolymer is linear in chain length in the liquid state or in the crystalline state. For the crystallize case, he found that the MWD is the FS distribution [Eq. (5)]. For the liquid case, he found a broader distribution (the “Lundberg distribution”),⁴

$$n_x^L = Lq^{x-1}(1-q)/x, \quad (8)$$

where $q = 1 - (M^0/M_w)$ and M^0 is the molecular weight of the monomer. Equation (8) is broader than the FS distribution, and has a PDI of $\ln(M_w/M^0)$. Peebles⁴ states (without references) that the “Lundberg distribution is also a result of extreme deviations from ideality.”

The issue of equal reactivity was addressed by Kaufman,²³ who considered the statistical mechanics of equilibrium polymerization on the equivalent-neighbor (mean-field) lattice and obtained the exponential distribution for the

case of fugacities independent of x , but obtained a “gamma” or “Schulz”-like distribution^{24,25} for the case of the fugacities with a power-law dependence on x ,

$$n_x^K = c d^{x+1} (x+1)^{R-1}, \quad (9)$$

where c is a normalization constant, d is a number less than unity and related to the fugacity, and R is the “Schulz index.” For $R \geq -1$, the distribution reduces to the FS distribution; equal reactivity corresponds to $R = 1$. For $R = \infty$, it reduces to the Poisson distribution. For $R < -1$, there exists a critical polymerization line.

Scaling arguments lead to the exponential distribution in the mean-field limit.²⁶ However, for the non-mean-field case, scaling arguments predict (a) the exponential distribution in the semidilute regime, and (b) a Schulz–Zimm-like distribution (i.e., a power law times an exponential) in the dilute regime,^{27–29}

$$n_x^{\text{SCALING}} = [\gamma^\gamma / L \Gamma(\gamma)] (x/L)^{(\gamma-1)} \exp(-\gamma x/L), \quad (10)$$

where $\gamma (=1.16)$ is the susceptibility exponent for the universality class with a dimension of the order parameter of zero ($n=0$).³⁰

In 1991, Bouchaud *et al.*³¹ proposed a “semiphenomenological” distribution to include the effects of correlations on the MWD, a form which was used in 1998 by Rouault³² to describe the MWD of a micelle system, which is similar to a living polymer system in that the polymeric entities are in equilibrium with one another and with the monomer. Rouault suggests that the polydispersity of such systems allows the smaller polymers to swell the larger ones, causing a different form for the MWD of a living polydisperse system,

$$n_x^{\text{POLY}} = c x^{-2\sigma} \exp(-x/L), \quad (11)$$

where c is a normalization constant and the exponent σ is found to be 0.25 both in a very indirect experiment³¹ and in a computer simulation.³²

Non-mean-field effects were also studied by Schäfer,³³ by renormalization group methods. He assumed that the chemical potential is linear in chain length; i.e., that the energy of polymerization is independent of chain length. His analysis excludes the gamma/Schulz distribution [Eq. (9)], and produces a complicated distribution function which in the semidilute limit “reduces to an exponential distribution, modified by power-law prefactors in the extreme wings.” On the other hand, he notes that this theory is valid only up to 10 weight per cent polymer and for $x \geq 500$.³⁴

The full time development of the MWD has also been reconsidered since BS. First, in 1965, Miyake and Stockmayer (MS)³⁵ assumed k_p and k_d to be independent of chain length, solved numerically the kinetic equations for a batch polymerization, and plotted such parameters as $[M]$, the PDI, M_n , and M_w , as functions of time. Their results confirmed the three stages listed by BS. In addition, they treated depropagation in the middle stage as a small perturbation on the propagation, and predicted that, for long chains, the time required for the crossover from the Poisson MWD to the Flory–Schulz MWD is proportional to L^2 . Further comments on the intermediate stages were made by Nanda and co-workers.^{36,37}

In 1984 Taganov³⁸ addressed anew the issue of the time development of the MWD in reversible polymerization, assuming that the polymer chains are long, the initiation is instantaneous, and the rate constants do not depend on chain length. His analysis also predicts a Poisson distribution in the beginning and a Flory–Schulz distribution at equilibrium, with a Gaussian distribution convoluted with the Poisson distribution for the intermediate stage.

In 1997, Milchev *et al.*¹⁹ studied the relaxation kinetics of a living polymer system both by numerical solution of rate equations like Eqs. (1)–(3), and by Monte Carlo simulations. They focused on a system for which the number of polymers is determined by an initiation step that is not complete and not irreversible, but argued that there is no significant difference if the number of polymers is fixed. They considered the change in L as a function of time for either (1) an initiated system of dimers subjected to a temperature jump, or (2) an equilibrated system of polymers subjected to a temperature jump. They confirmed Taganov’s results on the time evolution of the functions for the MWD. In addition, they found that the response curves scale with relaxation times that depend on the equilibrium values of L , and that the time required for stage 3, the relaxation to the final MWD, scales as L^5 . Recall that MS predicted that the relaxation time for step 3 scales as L^2 . Marques *et al.*³⁹ also studied the relaxation of a polymer chain after a temperature jump by the gain or loss of monomers from the ends, and predicted that the time required scales as L^2 .

There has never been an experimental test of these theories. We present here such a test. We consider the anionic polymerization of α -methylstyrene in tetrahydrofuran (THF), with sodium naphthalide as the initiator.⁴⁰ We have previously studied other properties of this system near the ceiling temperature: the mass density,⁴¹ the structure by small angle neutron scattering,⁴² the extent of polymerization as a function of temperature,⁴³ the shear viscosity,⁴⁴ the heat capacity,⁴⁵ and the chemical kinetics.⁶ We have also reviewed the issues in the physical chemistry of such systems.^{46–48}

II. COMPUTER MODEL

In a previous paper,^{6,49} we have described a numerical solution of the kinetic equations for the mechanism shown in Eqs. (1)–(3). We take the case in which the initiation reaction has been allowed to proceed to completion above the ceiling temperature, so that the concentration of initiated species is constant, and Eq. (1) above does not enter. We assume that the initiated dimer is the smallest propagating species and does not revert to monomer.^{40,50} The propagation reaction is then begun by quenching to a temperature below the ceiling temperature. For this situation, we can then solve Eqs. (3) numerically. We use values of k_p and k_d from our own experiments,⁶ and we take those rate constants to be independent of the degree of polymerization.

In Fig. 1, we plot the expected relaxation of L and M_w , as obtained from this computer model, using the values of k_p and k_d appropriate to the experiment to be described below (batch III).⁶ This calculation predicts that L (or M_n) will

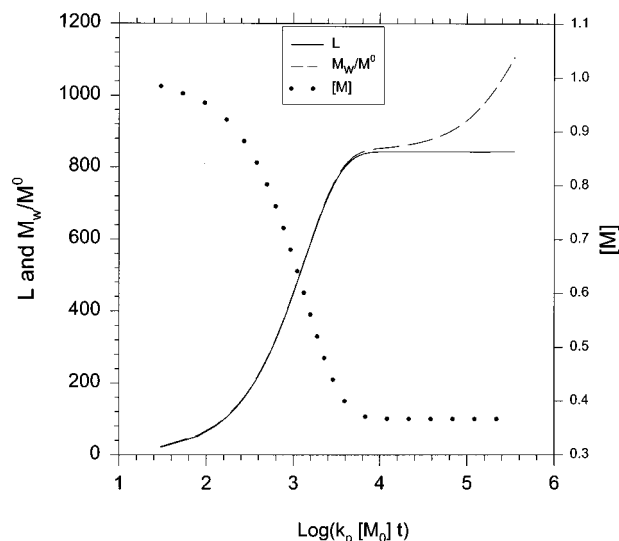


FIG. 1. Numerical solutions to the kinetic equations for the case in which (1) the initiation reaction proceeds to completion above the ceiling temperature, and thus the concentration of initiated species is constant; (2) the initiated dimer is the smallest propagating species and does not revert to monomer; (3) the propagation reaction is begun by quenching to a temperature below the ceiling temperature; (4) the rate constant is independent of chain length. Here L is the number average degree of polymerization, M_w is the weight average molecular weight, M^0 is the molecular weight of the monomer, $[M_0]$ is the initial monomer concentration, $[M]$ is the concentration of free monomer, k_p is the rate constant for propagation, and t is the time in seconds.

relax at the same rate as $[M]$, but that M_w will require an extremely long time.

III. EXPERIMENTAL TECHNIQUES

We prepared batches of monomer-initiator-solvent mixture, made a number of identical, sealed samples from each batch, put the samples into a temperature-controlled bath at a temperature below T_p , terminated the living polymer samples at that temperature after particular reaction times, and analyzed the samples for (1) concentrations of residual monomer and (2) for molecular weight distributions. We have previously discussed the residual monomer concentration as a function of temperature⁴³ and of time.⁶ Here we discuss the molecular weight distribution as a function of temperature and of time.

A. Sample preparation

Polymer synthesis by anionic polymerization requires assiduous attention to technique. Our procedures for preparing living poly(α -methylstyrene) have been described previously.^{6,41,43,49,51} Starting materials were 99% α -methylstyrene, 99.9% THF, and 99.5% sodium (all from Aldrich Chemical Co.), and 99% naphthalene (Baker Analyzed). We follow standard practices to eliminate water and air from the reaction system.^{52,53} Materials were handled in a vacuum line or a high purity glove box. The monomer had a final drying over sodium mirrors; the solvent had a final drying over sodium/potassium alloy. Sodium was the limiting reagent in the preparation of the naphthalide initiator solution, since sodium can itself initiate the polymerization

of α -methylstyrene.⁷ The initiator solution was used within 24 h of preparation. The final samples were sealed into glass cells. The samples were never cooled below T_p during their preparation or storage; this ensured that no polymers had ever been formed, and thus that no terminated polymers had been formed. The samples discussed here were not even frozen in order to seal the cells.

After sealing, the samples discussed here were aged for 3–4 months at room temperature, with the intention that any impurities present would be scavenged by the initiated dimer. There is a likelihood that some of the initiated dimers were terminated on one end only by impurities, producing a propagating species with one active end rather than two; we will show below that there was no evidence of significant partial termination. It is also possible that during such extended aging, chain transfer to monomer could take place; we will show below that there is evidence that chain transfer occurred.

The deliberate final termination must be accomplished in the absence of oxygen, because oxygen forms polymer radicals which can couple to make larger polymers.⁵⁴ Thus the samples were terminated (as detailed previously^{6,43}) via a glass break-seal to admit degassed wet tetrahydrofuran (THF).

Table I shows the samples we discuss here. We studied one batch of samples (batch III) as a function of reaction time at constant temperature; this set of samples is the same set used in our study of the chemical kinetics of this system and is labeled the same in that paper.⁵ We also studied one batch (batch II) as a function of temperature at constant reaction time; this set of samples is the same set used in our study of the extent of polymerization, but is labeled batch II, samples 4–9 in that paper.⁴³

The cells were held in a water/ethylene glycol bath, the temperature of which was controlled to a few mK⁵⁵ and measured with a precision of 1 mK and an accuracy of 10 mK using a digital platinum resistance thermometer (Model 9540B, Guildline Instruments, Orlando, FL).

Anionic polymerization is an exothermic chemical reaction, so there will be some “self-heating” by the sample as it polymerizes.⁵⁶ While the samples were not themselves stirred to dissipate heat, they were in a well-stirred bath. We estimate that for a 2 mL sample of monomer, initiator, and solvent, if all the monomer polymerized at once and if all that heat remained in the sample, then the sample temperature would increase by 23 K! However, for our experiments, the polymerization is incremental, a maximum of 60% of the polymer is finally polymerized, and the heat is allowed to dissipate into the bath. Even for the case of instantaneous and complete polymerization, we estimate that less than 2 min would be required for heat dissipation.

Because of the time required for the bath to regain temperature equilibrium after the introduction of the cells, there was some ambiguity about the start of the polymerization, which introduced an uncertainty of about 8 min in the reaction time.

TABLE I. Samples of living poly(α -methylstyrene) in tetrahydrofuran with sodium naphthalide as initiator. The mole fraction of initial monomer in solvent is x_m^0 . The concentration of initial monomer, M_0 , is 1.7 mol/L for all samples. The ratio of moles initiator to moles initial monomer is r . T_p is the polymerization temperature for that batch (Refs. 6, 43, and 47); its error is estimated at the 99% confidence interval. T is the temperature at which that cell was equilibrated. The time is the equilibration time; the uncertainty in the time is 4–8 min. L is the number average degree of polymerization from the debroadened data. M_w and M_n are the weight and number average molecular weight. L and M_w were determined from the debroadened data and have uncertainties of about 10%. The expected equilibration time is t . PDI is the polydispersity index (M_w/M_n), given for the broadened (b) and debroadened data (db).

| Sample | x_m^0 | r | T_p (K) | T (K) | Time (h) | L | $M_w \times 10^4$ | t (h) | PDI(b/db) |
|--------|-----------------|--------------|-------------|---------|----------|-----|-------------------|---------|---------------|
| III-65 | 0.146 80 | 0.0025 | 286 ± 2 | 266.961 | 0.5 | 211 | 3.33 | | 1.49/1.33 |
| 66 | $\pm 0.000\ 02$ | ± 0.0001 | | 266.961 | 1.0 | 214 | 3.86 | | 1.62/1.53 |
| 67 | | | | 266.971 | 0.8 | 223 | 3.83 | | 1.63/1.46 |
| 68 | | | | 266.973 | 2.0 | 296 | 5.67 | | 1.57/1.62 |
| 69 | | | | 266.959 | 4.0 | 300 | 6.13 | | 1.82/1.73 |
| 70 | | | | 266.957 | 8.0 | 333 | 7.16 | | 1.94/1.82 |
| 72 | | | | 267.063 | 20.0 | 339 | 7.46 | | 2.02/1.86 |
| II-44 | 0.144 50 | 0.0046 | 286 ± 2 | 264.642 | 20.0 | 137 | 2.88 | 14 | 2.11/1.78 |
| 45 | $\pm 0.000\ 02$ | ± 0.0001 | | 268.149 | 20.0 | 80 | 1.74 | 5 | 2.05/1.85 |
| 46 | | | | 271.723 | 20.0 | 84 | 1.73 | 5 | 1.81/1.74 |
| 47 | | | | 275.286 | 20.0 | 66 | 1.12 | 3 | 1.69/1.45 |
| 48 | | | | 278.882 | 20.0 | 36 | 0.75 | 1 | 1.72/1.78 |
| 49 | | | | 282.702 | 20.0 | 42 | 0.93 | 1 | 1.73/1.89 |

B. Sample analysis

Samples were analyzed by size exclusion chromatography (SEC). The samples were diluted with inhibitor-free THF and analyzed on a Model 150-C ALC/GPC Waters chromatograph, using a Jordi mixed bed column and an ultraviolet detector at 275 nm.

The raw chromatograms are shown in Fig. 2. Figure 2(a) shows the time series; Fig. 2(b) shows the temperature series. The figures center on the polymer peak, with a peak due to residual monomer shown to the right of the polymer peak. For the time series, the polymer peaks are well resolved from the monomer peak, each peak is unimodal, and the peaks show evidence of a low molecular weight (longer time) side band (discussed below). For the temperature series, samples II-44 to 46 are well resolved from the monomer peak and unimodal; samples 47 and 48 show some interference from the monomer peak, and sample 49 is considerably compromised by the monomer peak. We note that the monomer peak is not constant for samples 44–49, because the amount of residual monomer increases as the temperature nears T_p .

The SEC column was calibrated with nine poly(styrene) (molecular weights (MW)=640, 3300, 9400, 28 700, 66 000, 158 000, 321 000, 1 028 500, and 1 050 000), and two poly(α -methylstyrene) (MW=11 000 and 696 000) standard samples, and toluene (MW=98). A function cubic in the elution time was fitted to the logarithm of the molecular weights of the standards, using nonlinear least-squares fitting techniques:⁵⁷ $\ln(\text{MW}) = (31 \pm 18) - (1.9 \pm 0.1)t + (0.069 \pm 0.001)t^2 - (1.19 \pm 0.008) \times 10^{-3}t^3$, where t is the elution time/volume and the uncertainties are one standard deviation; residuals were random.

The chromatograms were then converted to molecular weight distributions using the conversion procedures described in the literature,^{58–60} as implemented by the computer program of Ballard.⁶¹ The program automatically corrects for the baseline drift⁶² by “drawing a straight line

between the lowest points on either side of the largest peak.”

The program corrects for the instrumental broadening of the peaks by using the broadening of a monodisperse (e.g., monomer) peak to estimate the broadening of other peaks; since broadening increases with molecular weight, this method underestimates the broadening of the polymer peaks.

The tabulated number distributions after debroadening are available from AIP as electronic files.⁶³

IV. RESULTS AND DISCUSSION

A. Time development of the MWD

We consider first the MWD as a function of time,⁵¹ as determined from batch III, samples 65–72 (see Table I). This experiment was done at a temperature 21 K below T_p .

Figure 3 shows n_x versus DP for all seven samples, as determined from the debroadened data, and with the same abscissa scale for ease of comparison. Below $\text{DP} \approx 25$, the data are very sensitive to the baseline correction and thus the “turn downs” in the data in that region should be considered instrumental artifacts.

For batch III, there is a low molecular weight species evident in the chromatograms [Figs. 2(a), at about 24 min] and in the number distributions (Fig. 3, at $\text{DP} \sim 100$ –150). On first thought, one expects that this peak must be due to partial termination of the bifunctional polymer. However, if there are unifunctional species present, then the bifunctional species have at most twice the average DP of the unifunctional species,^{64,65} whereas our data show a species with about 1/4 the average DP of the main species. Indeed, there is no evidence for either batch II or batch II of peaks due to partial termination. What can this low DP species be? By contrast, batch II shows no such low DP peak [see Figs. 2(b), 6–11).

Recall that these living polymers have anionic end groups, with associated sodium counter ions.^{46,47} Ruiz-

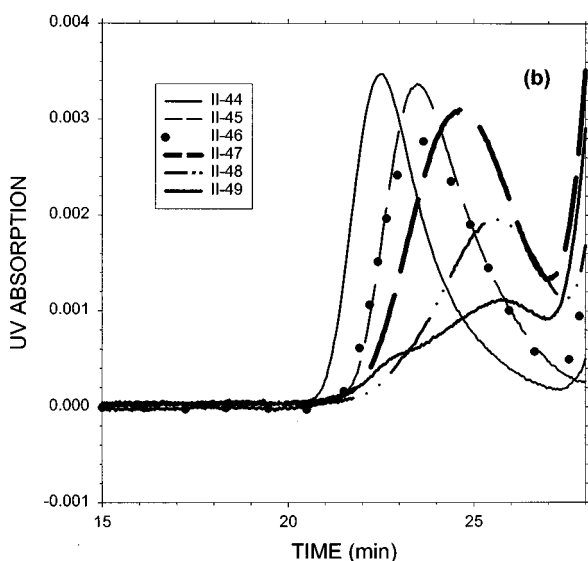
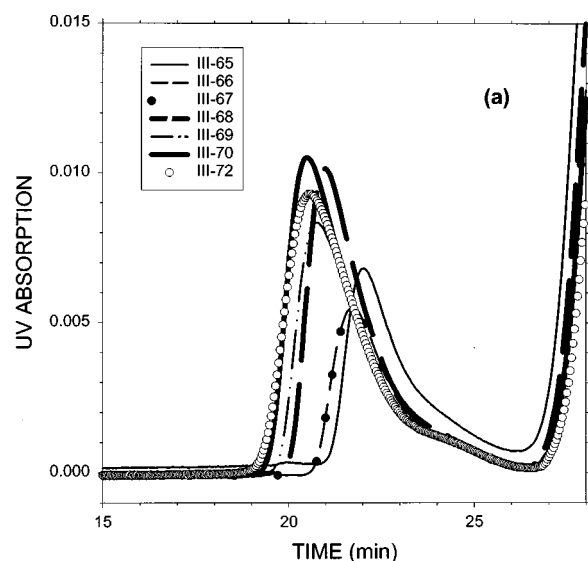


FIG. 2. Size exclusion chromatograms, ultraviolet (uv) absorption versus retention time, for poly(α -methylstyrene) samples: (a) shows the time series; (b) shows the temperature series. For both cases, the figure centers on the polymer peak, with a peak due to residual monomer at the right of the polymer peak.

Garcia and Castillo⁶⁶ (RG-C) report observations by dynamic light scattering of considerable Coulombic aggregation in these solutions of living poly(α -methylstyrene) in THF, analogous to that reported for living poly(styrene) in benzene.⁶⁷⁻⁷⁰ Above T_p , RG-C believe that the dimers form “long, linear association(s),” and that these linear associations then dissipate when the temperature is lowered below T_p . They did not measure the time required for this dissipation, but do note that this required less than 3 h. Thus it is possible that our assumption of complete initiation is not entirely true, and that the initiated species are not immediately free to propagate on cooling below T_p . Then some of the initiated species will start propagating later, and generate polymers of smaller DP, as seen in batch III. These low DP species do seem to dissipate

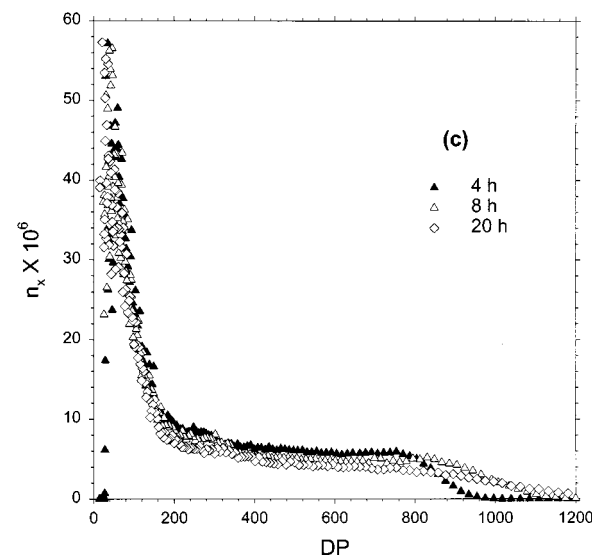
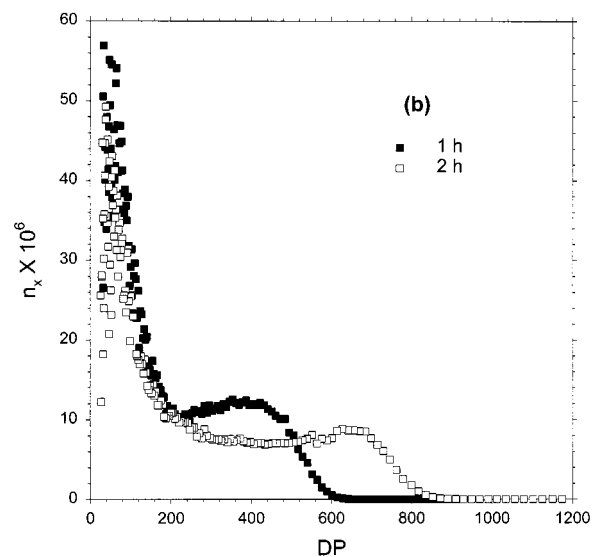
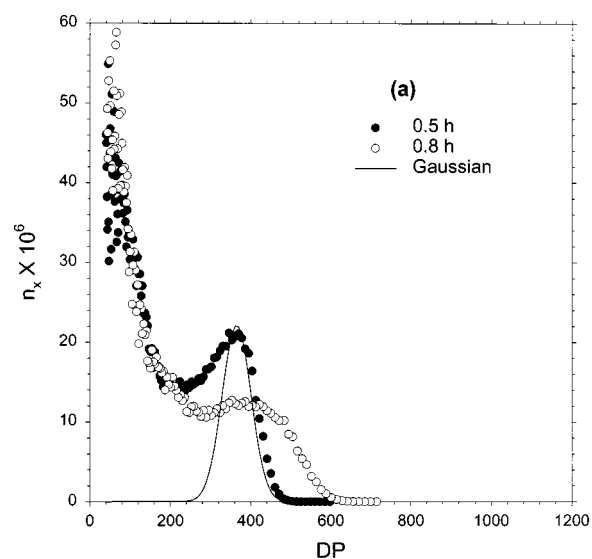


FIG. 3. Molecular weight distribution as a function of time from samples III-65 to III-72: Number fraction, n_x , versus degree of polymerization, DP, at seven reaction times (batch III, Table I). In (a), a transitional Gaussian distribution is indicated for the 0.5 h sample.

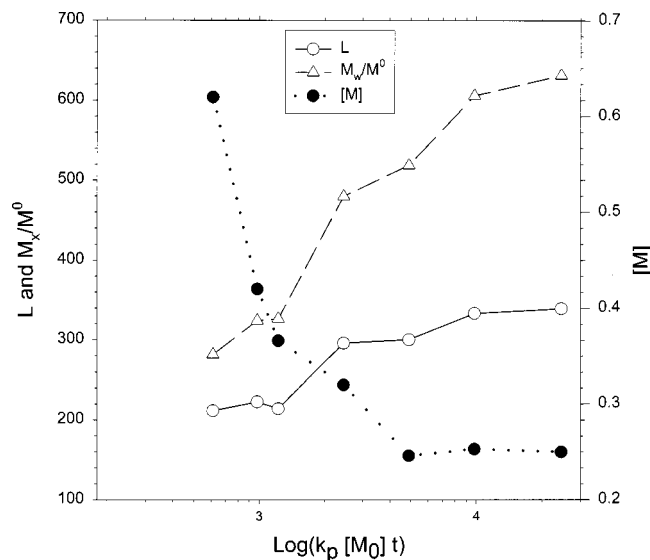


FIG. 4. L and (M_w/M^0) as functions of reduced reaction time; also plotted is the fraction of initial monomer remaining, $[M]$, as reported previously (Ref. 6). Compare Fig. 1.

slowly with time, and are not very visible at 20 h. Since batch II samples were all equilibrated for 20 h, the effects of such delayed initiation could have equilibrated away for batch II.

Figure 3 is to be compared to Fig. 2(b) of Milchev *et al.*¹⁹ We do not have data at an early enough time to see the initial Poisson distribution. However, we do see evidence [Fig. 3(a)] of a transitional Gaussian distribution, as predicted by Taganov³⁸ and by Milchev *et al.*,¹⁹ followed by the slow dissipation of that intermediate state as equilibrium is approached.

Figure 4 shows L and (M_w/M^0) from the experiment, where M^0 is the monomer molecular weight, as a function of reduced reaction time, where $k_p = 0.20$ L/mol s and the initial monomer concentration $[M_0] = 1.7$ mol/L.⁶ L and (M_w/M^0) were calculated by including all the data in the MWD's; that is, all the data in each plot of Fig. 3. Also plotted in Fig. 4 is the fraction of initial monomer remaining at each time, as reported previously.⁶ We first note that while the monomer concentration, $[M]$, equilibrated fairly rapidly (about 4 h), both L and (M_w/M^0) required much more time to equilibrate, even more than the 20 h over which measurements were made. This difference is not consistent with the expectations of Brown and Szwarc⁹ and of Miyake and Stockmayer,³⁵ who predicted that L would equilibrate at about the same rate as the monomer concentration. This is also not consistent with our own numerical solution of the rate equations (Sec. II), as a comparison of Figs. 1 and 4 shows. However, this delay in the equilibration of the MWD could be related to a delayed initiation and propagation due to Coulombic aggregation.

Second, we emphasize that L and (M_w/M^0) were not yet equilibrated after 20 h at $T_p - T = 21$ K. Miyake and Stockmayer estimated that the redistribution process would require a time of $1/2k_d r^2$, where r is the ratio of initiator concentration to monomer concentration. For our sample ($r = 2.5 \times 10^{-3}$, $k_d = 0.085$ s⁻¹)⁶ this gives an equilibration

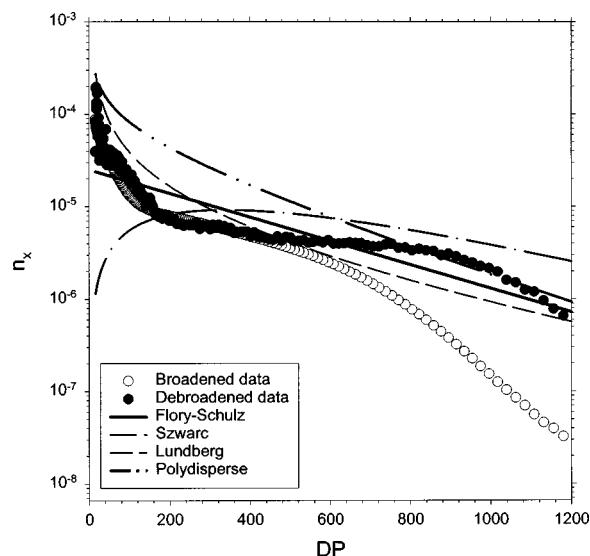


FIG. 5. For sample III-72 at 20 h, the number fraction of polymers of degree of polymerization x , n_x , versus degree of polymerization, DP, compared to the various theoretical equilibrium distributions, as indicated in the legend. The data are shown both before and after the debroadening correction.

time of 260 h. In Fig. 5, we compare the data at 20 h to the various predicted equilibrium distributions. Here and in the figures to follow, we plot the data both before and after the debroadening correction. Also here and in the figures to follow, the exponential [Eq. (6)] and the scaling [Eq. (10)] predictions for the MWD are indistinguishable from the Flory-Schulz prediction [Eq. (5)], so we plot only the Flory-Schulz prediction; all theoretical distributions are calculated using the experimental values for L (see Table I). Figure 5 indicates that the data are not described by any of the theories, since equilibrium was not yet attained after 20 h at this temperature. However, the data are consistent with a final Flory-Schulz distribution.

B. Temperature dependence of the MWD

We consider now the equilibrium MWD as a function of temperature, as determined from batch II, samples 44–49 (labeled II-4 to II-9 in Das *et al.*⁴³ and listed in Table I). This experiment was done at temperatures from 3 to 21 K below T_p , with a reaction time of 20 h for each sample. We expect equilibration times to be shorter at temperatures closer to T_p , where depropagation competes more effectively with propagation to achieve the equilibrium MWD. We do not know the rate constants at these various temperatures, so we cannot estimate relaxation times.³⁵ However, we can use the predictions (see Sec. I) that relaxation times scale as L^2 or as L^5 . For sample 72 in the time series, we estimated (see above) a relaxation time of 260 h; the appropriate L is the equilibrium L , which we estimate as $(2/r)$ times the equilibrium extent of polymerization of 0.75⁶ to give $L = 600$. If the equilibration times scale as L^2 , then we obtain the times listed in the last column of Table I, all of which are less than 20 h. If the times scale as L^5 , then we get even shorter times. Thus we could expect that all these samples would be essentially equilibrated.

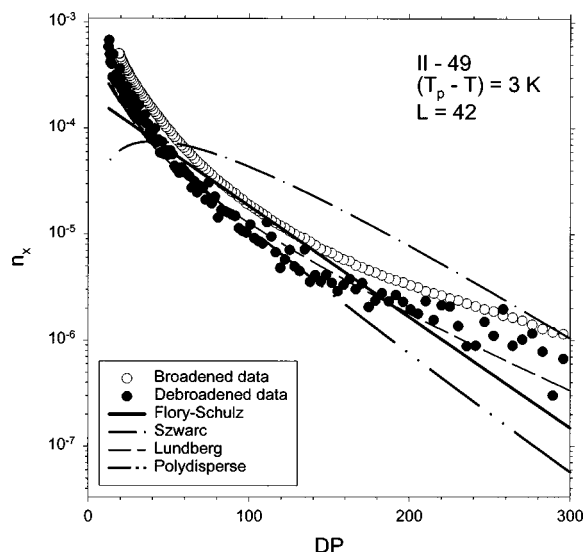


FIG. 6. Molecular weight distribution for sample II-49: The number fraction of polymers of degree of polymerization x , n_x , versus degree of polymerization, DP, compared to the various theoretical equilibrium distributions as indicated in the legend. The data are shown both before and after the debroadening correction.

In Figs. 6 to 11, we show the logarithm of n_x versus DP for each sample, as compared to the various theoretical predictions. We note the following:

- (1) The number average degree of polymerization, L , for each sample is derived from the molecular weight distribution and has an uncertainty of 5%–10%, which explains why L is sometimes smaller when $(T_p - T)$ is larger (see Table I).
- (2) Recall also that at DP less than about 25, baseline errors can distort the data [see Figs. 7(b) and 8(b)], and that for sample II-49, Fig. 6, the chromatogram in Fig. 2(b) indicates that the MWD data are compromised by the overlapping monomer peak, which would cause n_x to be increased above its true value, especially at low DP.
- (3) The data for $(T_p - T) \leq 18$ K (Figs. 6–9) are closer to the theoretical predictions than are the data for $(T_p - T) > 18$ K (Figs. 5, 10, and 11). We assume that this is because the data closer to T_p are better equilibrated. Figures 10 and 11 suggest that samples II-44 and 45 were not equilibrated after 20 h, despite the calculation discussed above. Again, the delayed equilibration can be a result of the Coulombic aggregations discussed above.
- (4) The Szwarc distribution, Eq. (7), does not describe the data at any temperature. However (see below), if there were considerable chain transfer, the polymer chains could have been converted from two active sites to one active site each, so our results do not disprove Szwarc's equation.
- (5) The best data (i.e., not compromised by the monomer peak and seeming to be equilibrated) are for samples 46, 47, and 48. The best descriptions of the best data are the “polydisperse” distribution, Eq. (11), for $L \leq 66$ (samples 47 and 48), and the FS equation for $L > 66$ (sample 46). The polydisperse equation is plotted with σ fixed at 0.25 and with “c” as a free parameter; if both σ

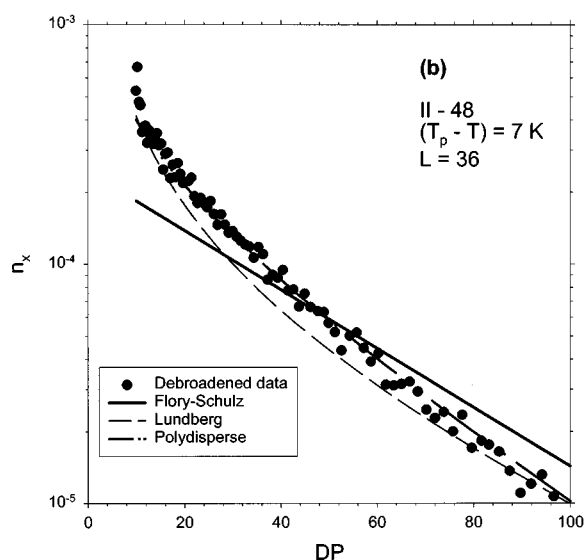
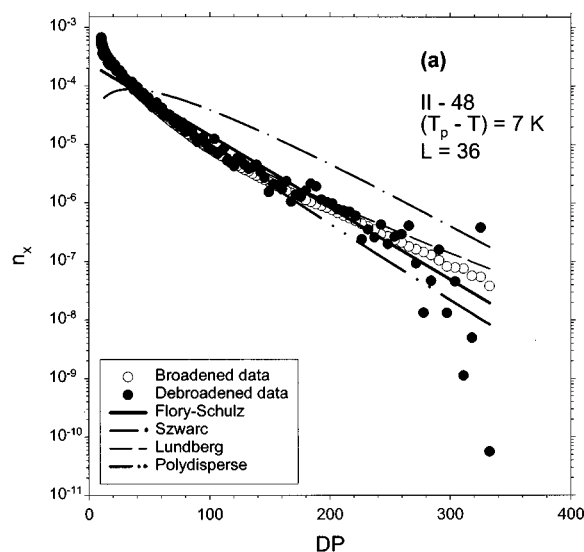


FIG. 7. Molecular weight distribution for sample II-48: The number fraction of polymers of degree of polymerization x , n_x , versus degree of polymerization, DP ($=x$), compared to the various theoretical equilibrium distributions as indicated in the legend. Part (a) is the full data set, before and after the debroadening correction; part (b) shows the data for $DP \leq 100$.

and “c” are allowed to be free parameters, the values obtained for σ are in the range 0.4 to 0.5, which do not correspond to earlier reports.³²

- (6) The Flory–Schulz/scaling/exponential equation [Eqs. (5), (6), and (10)] describes the data better as L increases (Figs. 9 and 10 and also 5 and 11), and as DP increases for a given L (Fig. 7). Figure 8 is anomalous in this regard, perhaps because L is at the cross over between the Flory–Schulz regime and the polydisperse regime.
- (7) The Lundberg equation has the right behavior in every case except for $L=66$ at high DP [II-47, Fig. 8(a)].
- (8) Preliminary results indicate that the Kaufman distribution will also describe the data for $(T_p - T) \leq 7$, but this distribution has three free parameters and thus too many degrees of freedom for a meaningful analysis.
- (9) We can calculate the expected value of the number average degree of polymerization: $L_{\text{calc}}(T) = 2\phi(T)/r$,

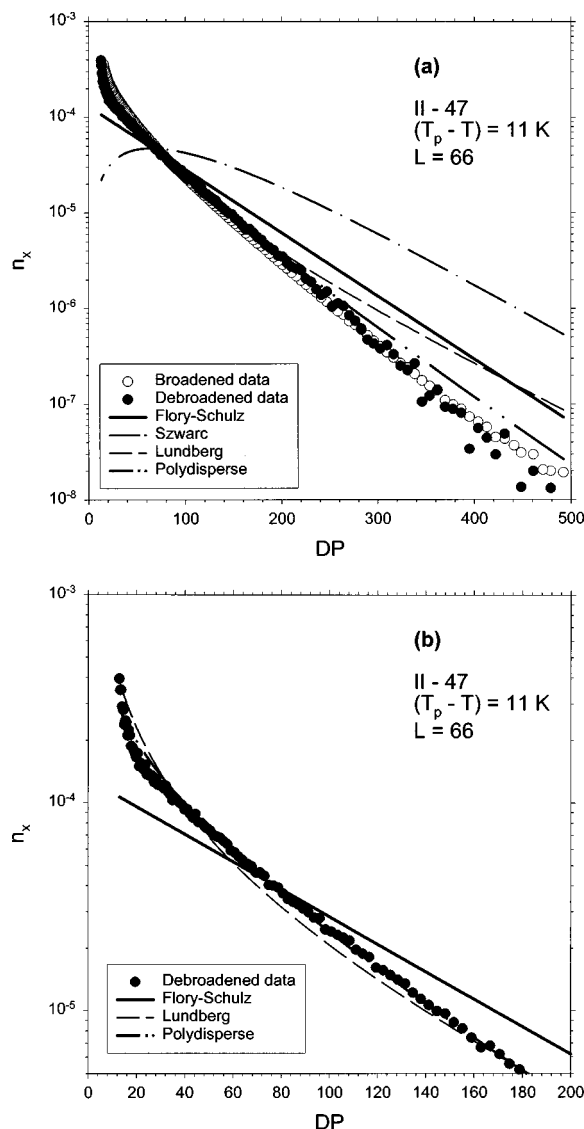


FIG. 8. Molecular weight distribution sample II-47: The number fraction of polymers of degree of polymerization x , n_x , versus degree of polymerization, $DP (=x)$, compared to the various theoretical equilibrium distributions as indicated in the legend. Part (a) is the full data set, before and after the debroadening correction; part (b) shows the data for $DP \leq 200$.

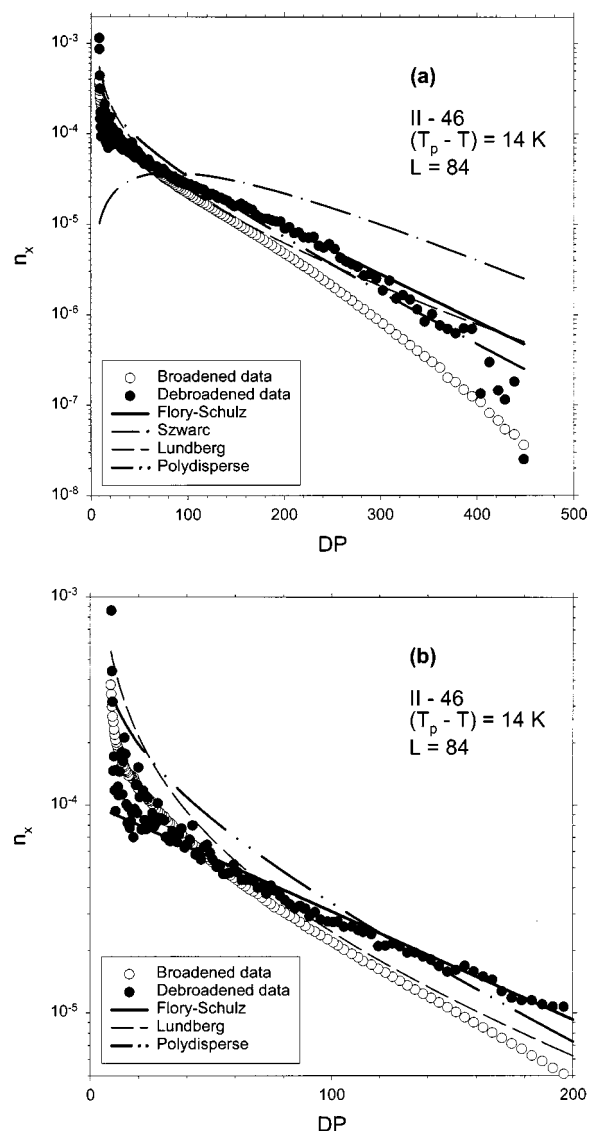


FIG. 9. Molecular weight distribution sample II-46: The number fraction of polymers of degree of polymerization x , n_x , versus degree of polymerization, $DP (=x)$, compared to the various theoretical equilibrium distributions as indicated in the legend. Part (a) is the full data set, before and after the debroadening correction; part (b) shows the data for $DP \leq 200$.

where $\phi(T)$ is the extent of polymerization at equilibrium at T .^{11,71} If many of the original initiators were completely terminated, then $L_{\text{expt}}(T)$ as measured experimentally would be larger than L_{calc} , since fewer polymers would have developed. If many of the original initiators were half-terminated, then $L_{\text{expt}}(T)$ should still equal L_{calc} , since the same number of polymers would have been formed. We can calculate $L_{\text{calc}}(T)$ using the $\phi(T)$ measurements made on these very samples.⁴³ Figure 12 shows $L_{\text{calc}}(T)$ and $L_{\text{expt}}(T)$ for batch II. $L_{\text{expt}}(T)$ is about a factor 2 less than $L_{\text{calc}}(T)$ for every sample!

How can $L_{\text{expt}}(T)$ be less than $L_{\text{calc}}(T)$? We can think of the following reasons:

- The system is not yet at equilibrium. Samples II-44 and II-45 show evidence of not being equilibrated, but we believe that II-49, 48, 47, 46 are equilibrated.
- The assumptions that the solutions are ideal and that the equilibrium constants for propagation are independent of DP are not true, and these conditions lead to a different $L(T)$.
- Coulombic aggregations (see Sec. IV A) affect the MWD. RG-C⁶⁶ see evidence of ionic aggregation in this system below T_p , in the form of micelles made of living polymers. It is conceivable that the equilibrium L is achieved by a combination of covalent and Coulombic “bonds” which yield the appropriate equilibrium ϕ .⁴³ When the sample is terminated, the Coulombic “bonds” are neutralized, yielding fragments of the original “polymer.” We then measure the distributions of these fragments. We expect the measured rate constant for propagation to be smaller than in the absence of such aggregation, but we might not recognize this effect if the literature experiments also “suffered” from aggregation.

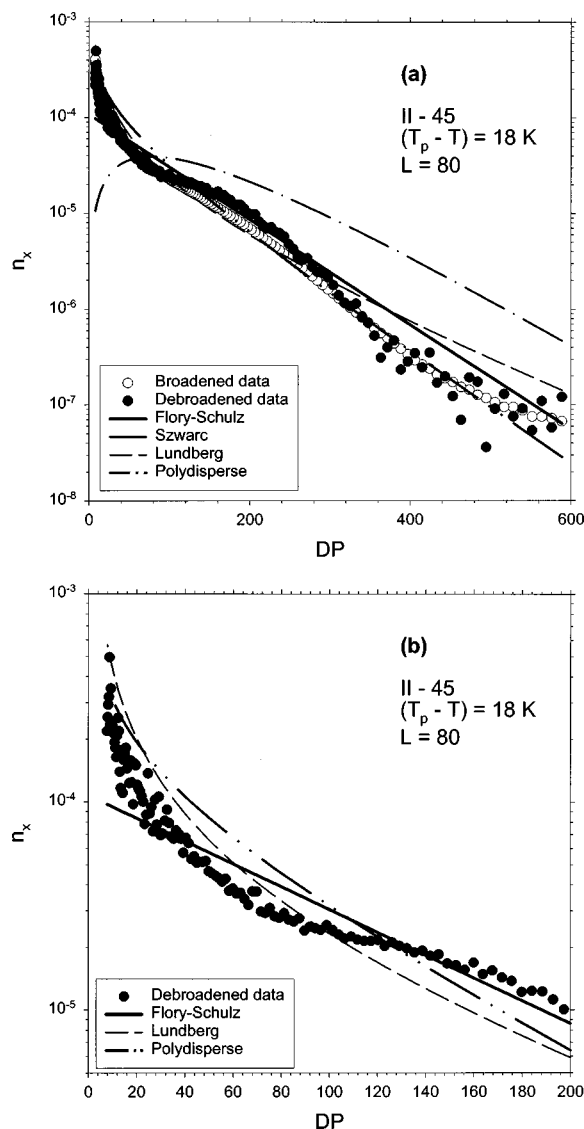


FIG. 10. Molecular weight distribution sample II-45: The number fraction of polymers of degree of polymerization x , n_x , versus degree of polymerization, $DP (=x)$, compared to the various theoretical equilibrium distributions as indicated in the legend. Part (a) is the full data set, before and after the debroadening correction; part (b) shows the data for $DP \leq 200$.

- (d) Our assumption of no chain transfer is not correct: During the aging of the samples above T_p , the initiated dimers could each have transferred an active site to a free monomer, resulting in twice as many activated species and thus half the expected L . It is generally assumed that chain transfer is not important for ionic polymerizations,⁷² but the aging of our samples before polymerization allowed much time for this reaction. A system of $2n$ chains with one active site will have a monomer reaction rate that is the same as that of a system n chains with two active sites, so we would see no apparent effect on the rate constant. If chain transfer were significant, it would be expected to affect L , but not to affect the nature of the equilibrium distribution.¹¹

- (e) The expression $L_{\text{calc}}(T) = 2\phi(T)/r$, where $r = [M_0]/[I]$, needs to be modified and r expressed as

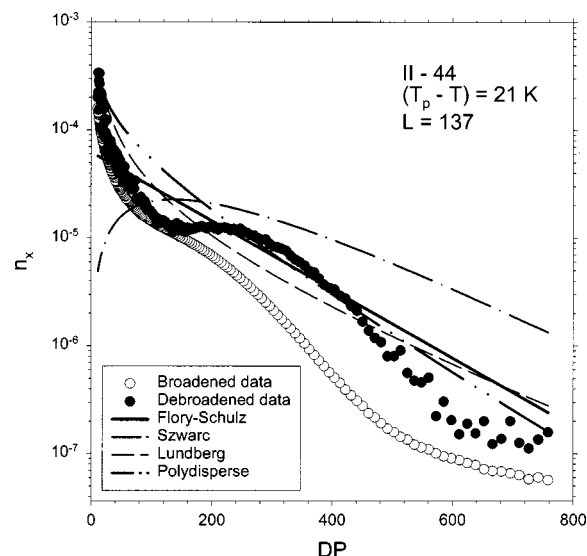


FIG. 11. Molecular weight distribution sample II-44: The number fraction of polymers of degree of polymerization x , n_x , versus degree of polymerization, $DP (=x)$, compared to the various theoretical equilibrium distributions as indicated in the legend. Data are shown before and after the debroadening correction.

volume fractions rather than mole fractions. This point of view results from considerations of a lattice model of a living polymer solution,^{11,73} and could lead to a discrepancy of the order observed.

V. CONCLUSIONS

The study of the molecular weight distribution (MWD) during equilibrium polymerization is a difficult task which, so far as we know, has not previously been attempted. There are the complications of handling samples extremely sensitive to air and water. There are the subtleties of the conversion of chromatograms to MWD's: column calibration, baseline correction, instrumental debroadening correction, peak

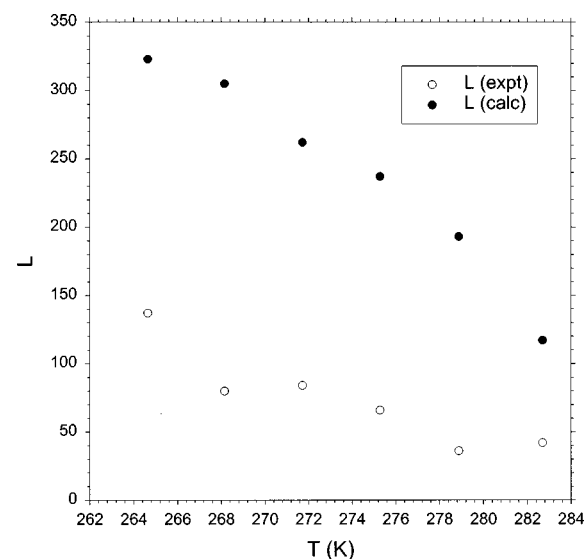


FIG. 12. For batch II, samples 44-49, the value of L calculated from $L(\text{calc}) = 2\phi/r$, where ϕ is the extent of polymerization and $r = [M_0]/[I]$, and the experimental value, $L(\text{expt})$, as functions of T .

interference. There are problems with long equilibration times and side reactions. We present here some progress on this task.

We have studied the time development of the MWD of "living" poly(α -methylstyrene) in tetrahydrofuran initiated by sodium naphthalide, after a quench to 21 K below the polymerization temperature. We observe a short-lived population of polymers with a number average degree of polymerization (L) of about one-fourth that of the main population. We observe an intermediate Gaussian distribution for the main population. We measure a longer equilibration time for M_n , as well as for M_w , than for the monomer concentration, $[M]$, whereas theories predict that M_n and $[M]$ will relax together and that M_w will take much longer. It is possible that the low L species and the equilibration of the MWD are related to the Coulombic aggregation of the charged living polymers, as reported by Ruiz-Garcia and Castillo.⁶⁶ The MWD seems to be approaching a Flory/Schulz/exponential distribution for the equilibrium state.

We have also studied the equilibrium (or near equilibrium) MWD of this system as a function of the difference in temperature from the polymerization temperature, where L increases as $(T_p - T)$ increases. For polymers with $L > 66$, we present evidence that the equilibrium MWD is an exponential/Flory-Schulz distribution, and is consistent with scaling predictions. For $L \leq 66$, we find deviations from the exponential/Flory-Schulz distribution, but the distribution proposed by Lundberg²² for nonideal systems, and that proposed by Bouchaud *et al.*³¹ for polydisperse systems both give good representations of the data. It is possible that the dependence of the equilibrium constant for propagation on chain length for small chains,²³ as indicated by the measured dependence of the enthalpy of propagation on chain length,⁵⁶ is also a factor.

The measured $L(T)$ is smaller than the value expected from the initial initiator concentration. We suggest a number of causes for this result, including the occurrence of considerable chain transfer, and the presence of Coulombic aggregations of the ionic chains.

ACKNOWLEDGMENTS

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