Macromolecules

Volume 8, Number 3 May–June 1975

The Reaction of *tert*-Butyllithium with Styrene and Isoprene. A Comparison of Chain Initiation with the Isomers of Butyllithium

J. E. L. Roovers and S. Bywater*

Division of Chemistry, National Research Council of Canada, Ottawa, Canada.

Received December 3, 1974

ABSTRACT: The rate of chain initiation by *tert*-butyllithium has been measured with the monomers styrene and isoprene. Both aliphatic and aromatic hydrocarbon solvents have been used. The results are compared with those obtained using the normal and secondary isomers. In hexane or cyclohexane, the behavior is very similar except that *n*-butyllithium is a very much slower initiator than are the branched chain isomers. In benzene the results with *tert*-butyllithium show that there is a region where the reaction is first order in initiator and zero order in monomer. Some possible explanations for this behavior, not so far observed with the other isomers, are examined.

The use of lithium alkyls as polymerization initiators provides an important method for the production of monodisperse polymers. Surprisingly large differences in initiation rates are observed between straight and branched chain lithium alkyls.[1,2] *sec*-Butyllithium, for example, initiates several powers of ten more rapidly than *n*-butyllithium in benzene. Less work has been carried out on *tert*-butyllithium. Hsieh has reported that in cyclohexane the order of efficiency (defined as more complete initiation at lower monomer consumption) is *sec*- > *tert*- > *n*-butyllithium for the dienes and *sec*- > *n*- > *tert*-butyllithium for styrene. These experiments were carried out using commercial products and it seemed of interest to repeat these experiments on purified materials as the reactions of lithium alkyls are known to be sensitive to impurities.

In addition the exchange reactions of *tert*-butyllithium with other alkyls are known to be slow[3,4] whereas those of *n*- and *sec*-butyllithium are considerably faster.[5] If, as suggested,[4] the slow exchange rate is determined by the rate of dissociation of the predominantly tetrameric *tert*-butyllithium, then it seemed likely that at least in benzene some differences in initiation behavior might be expected. In this solvent the initiation mechanism has been suggested to involve a prior dissociation of the aggregates.[6] The rate of addition of *tert*-butyllithium to 1,1-diphenylethylene has already been studied in benzene.[7] At very low monomer concentration, the reaction order in initiator was found to be 0.25 which suggests the dissociative mechanism holds under these conditions. We have, therefore, studied the reaction of *tert*-butyllithium with isoprene in benzene and hexane and with styrene in benzene and cyclohexane. The use of aliphatic hydrocarbon solvents produces quite different initiation behavior to that in aromatic solvents.[2]

Experimental Section

Monomer and solvent purification and the high vacuum techniques used have been described in earlier publications from this laboratory.[6,8,9] Commercially available *tert*-butyllithium (Foote Mineral Co., shipped in Dry Ice) was subjected to a short-path vacuum sublimation before distribution into fragile bulbs in the form of solutions. Examination of the ^{1}H NMR spectrum of the product showed, besides the strong band of the *tert*-butyl protons, a separate peak corresponding to about 4–5% of an impurity which may be *tert*-butoxylithium. Early experiments in hexane and cyclohexane were carried out with this product but later ones used initiator prepared from gas chromatographically pure *tert*-butyl chloride by a vacuum modification of the method of Kamienski.[10] (Later commercial samples available to us, shipped by normal methods, showed evidence of extensive decomposition on arrival. *tert*-Butyllithium solutions are not stable at room temperature and deteriorate on storage. Sublimation of this material gave an unacceptable product containing much more than 5% impurity. Although sublimation does improve the product it is clear that impurities are also volatile. This product was not used.) The laboratory product, after sublimation and dilution in the appropriate solvent, showed only 0.4% impurity signal. A cross-check on the isoprene–*n*-hexane system showed no kinetic differences greater than the experimental error between experiments using the two products. Larger amounts of *tert*-butoxylithium (of the order of the initiator concentration) produce changes in reaction rates. Solutions of *tert*-butyllithium were clear and colorless. No absorption maximum was observed down to 210 nm (*n*-hexane) although a shoulder was visible at 280 nm. The reaction rates were measured by monitoring the formation of polystyryl- or polyisoprenyllithium using their uv absorption. In the case of isoprene this involved a correction for the initial absorption of the *tert*-butyllithium. Since one molecule of *tert*-butyllithium disappears for each molecule of polyisoprenyllithium formed this is easily accomplished by decreasing the extinction coefficient of the latter by the extinction coefficient of *tert*-butyllithium at the same wavelength. No correction is required for styrene since the anion absorption band appears at appreciably longer wavelengths. GC evaluation of the polymers pro-

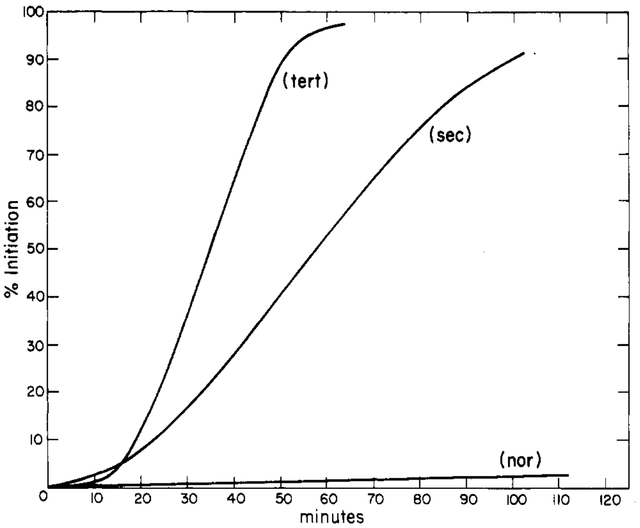

Figure 1. Conversion–time curves for the reaction of butyllithium with isoprene in *n*-hexane at 30°. [*t*-BuLi] = 1.02×10^{-3} *M*, [isoprene] = 0.204 *M*, [*s*-BuLi] = 1.03×10^{-3} *M*, [isoprene] = 0.14 *M*. [*n*-BuLi] = 7.54×10^{-4} *M*, [isoprene] = 0.355 *M*. Note that the monomer concentration varies. At constant monomer the secondary and tertiary rates would be more closely similar.

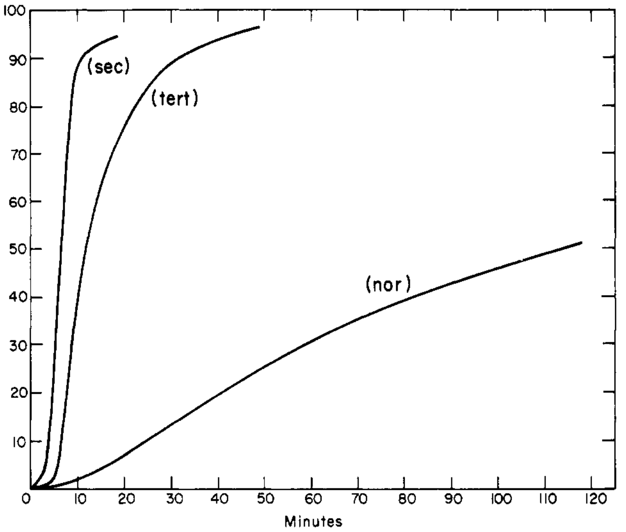

Figure 2. Conversion–time curves for the reaction of butyllithium with styrene in cyclohexane at 40°. [*t*-BuLi] = 1.10×10^{-3} *M*, [styrene] = 0.085 *M*, [*s*-BuLi] = 1.19×10^{-3} *M*, [styrene] = 0.093 *M*, [*n*-BuLi] = 9.95×10^{-4} *M*, [styrene] = 0.260 *M*. Note the much higher styrene concentration used for *n*-BuLi.

duced was carried out using a Waters Model 301 chromatograph equipped with eight 4-ft columns of nominal pore size 60, 500, 3×10^3, 10^4, 3×10^4, 10^5, 3×10^5, 10^6 Å. The solvent used was tetrahydrofuran. Both columns and detector were thermostated at 35°. Samples (4 mg) were injected via a 2-ml loop.

Results

(a) Hexane (Isoprene) or Cyclohexane (Styrene) Solvent. The reaction curves for *tert*-butyllithium showed the typical sigmoidal shape previously observed with *sec*- and *n*-butyllithium. It appears that the reaction is catalyzed by the products formed. Figure 1 shows typical conversion–time curves for isoprene with the three isomers of butyllithium at initiator concentrations ~10^{-3} molar in hexane. The overall reaction rate decreases in the order tert > sec ≫ normal. *n*-Butyllithium is very much less efficient and despite a monomer/initiator ([M]/[I]) ratio of almost 500 some initiator will remain after total monomer consumption. The initial reaction rate of *tert*-butyllithium is much smaller than that of *sec*-butyllithium. Attempts to measure it accurately failed because of this fact. The time required to reach an arbitrary 0.01 optical density (1-cm path) is, however, proportional directly to monomer and initiator concentrations so that it is likely that as for *sec*-butyllithium[9] the reaction is first order in both and corresponds to direct reaction of the tetramer with isoprene. Once a small amount of polyisoprenyllithium is formed the reaction rate increases markedly and at its maximum is about 30% higher than for the secondary isomer. At this point the apparent order with respect to initial initiator concentration is about 0.7, close to the value observed previously for the other isomers. Addition of an equimolar quantity of *tert*-butoxylithium (prepared by destruction of half the initiator with *tert*-butyl alcohol)[11] increases the initial rate but depresses the maximum rate. The net result is an appreciably slower overall initiation process.

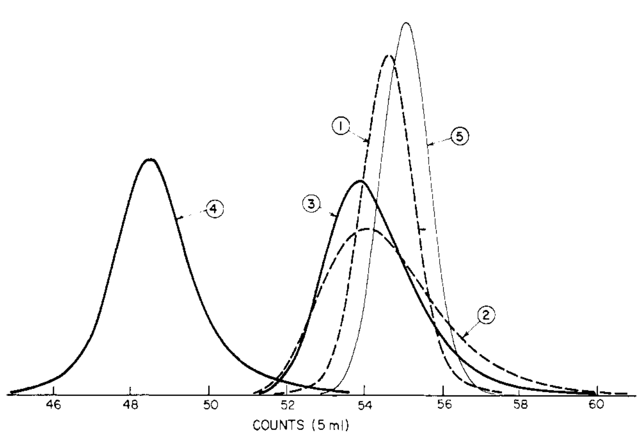

Figure 3. Gel permeation chromatograms of polystyrene produced under various conditions: (1) benzene solvent, [*t*-BuLi] = 3.9×10^{-3} *M*, [styrene] = $1.08 \times 10^{-2} + 3.75 \times 10^{-1}$ *M* (two steps); (2) benzene solvent, [*t*-BuLi] = 4.2×10^{-3} *M*, [styrene] = 4.0×10^{-1} *M* (one step); (3) cyclohexane solvent, [*t*-BuLi] = 5.0×10^{-3} *M*, [styrene] = 4.6×10^{-1} *M* (one step); (4) cyclohexane solvent, [*t*-BuLi] = 4.7×10^{-4} *M*, [styrene] = 4.0×10^{-1} *M* (one step); (5) benzene solvent, *s*-BuLi reference (one step).

The results for styrene (cyclohexane at 40°) are shown in Figure 2. In this case, the reaction rate decreases in the order sec > tert ≫ normal. The tertiary isomer has again a lower initial rate. The maximum rate is similar to that of *sec*-butyllithium, but the rate decreases more rapidly at conversions greater than 50%. *n*-Butyllithium is much less effective than the other two, contrary to the results of Hsieh. To obtain reaction rates of a convenient magnitude the [M]/[I] ratio is low and corresponds to the formation of polymer with *M* = 10,000. Despite these conditions which are unfavorable for complete initiation, both secondary and tertiary isomers will do so, only the normal isomer fails in this regard. This again does not agree with the results of Hsieh who failed to obtain complete initiation with *tert*-butyllithium at even higher [M]/[I] ratios. A confirmation of the fact that *tert*-butyllithium is a reasonably efficient initiator in cyclohexane can be obtained by gel permeation chromatography (Figure 3). A polystyrene of molecular weight ~10,000 can be prepared having an apparent M_w/M_n ratio of 1.27 (uncorrected for instrumental broadening). At a higher [M]/[I] ratio *M* = 100,000) the distribution narrows as expected to give an apparent ratio of 1.19. If on the other hand the commercial material is used directly a very asymmetric distribution with a very long low molecular weight tail is produced. Both the present work and that of Hsieh are therefore internally consistent. Use of impure *tert*-butyllithium gives products of broad molecu-

Table I
Rate of Initiation (R_i) of Isoprene by *tert*-Butyllithium in Benzene at 30°[a]

[*t*-BuLi], *M* stoichiometric	[M]/[I]	R_i, *M* sec^{-1}	$R_i/[\mathrm{BuLi}_4]^{1/4}[\mathrm{M}]$, $M^{-1/4}$ sec^{-1}
8.3×10^{-4}	0.21	1.05×10^{-7}	4.9×10^{-3}
1.4×10^{-3}	0.20	2.08×10^{-7}	5.4×10^{-3}
1.4×10^{-3}	0.62	6.0×10^{-7}	5.0×10^{-3}
1.4×10^{-3}	1.07	1.08×10^{-6}	5.6×10^{-3}
3.95×10^{-3}	0.18	6.3×10^{-7}	5.0×10^{-3}
9.54×10^{-3}	0.18	1.8×10^{-6}	4.8×10^{-3}

[a] Experiments at low monomer/initiator ratios.

lar weight distribution and slow initiation. On the other hand carefully purified material gives faster initiation and narrow distribution products. It is not clear what impurity in the commercial product could cause this discrepancy; it appears not to be *tert*-butoxylithium for in a 1:1 ratio this was found to reduce the induction period and to accelerate the overall rate of initiation of styrene contrary to the results obtained with isoprene. The instability of *tert*-butyllithium solutions is not, however, directly connected with chance oxidation of the solution to produce *tert*-butoxylithium. Even carefully purified dilute solutions in hexane held under vacuum soon develop a yellow coloration. This suggests metallation products are present in solutions stored for appreciable times at room temperature.

(b) Benzene as Solvent. In this solvent no autocatalysis occurs and rates were measured as before[6] from the initial rate of formation of the polymer anions. At low concentrations of isoprene, rates are several powers of ten faster than even the maximum rates in hexane or cyclohexane as is customarily found in these systems. Under these conditions rates are of fractional order in initiator and first order in monomer. It was difficult to determine the exact order in *tert*-butyllithium over a wide concentration range because the isoprene concentration must also be maintained at a value not greater than that of the initiator otherwise the kinetic behavior changes. A series of experiments was carried out at [M] < [I] (usually with a ratio of 0.2) where the rates are still proportional to monomer concentration. As shown in Table I these give consistent values of the overall rate constant assuming orders of 0.25 and 1 in initiator and monomer, respectively. The results are not sufficiently accurate to exclude fractional orders close to 0.25. With a large excess of monomer the rates become independent of its concentration. At this point the initiator order changes to about unity as shown in Figure 4.

The initiation rates for styrene with *tert*-butyllithium on the other hand are independent of monomer concentration over a much wider concentration range (Figure 5). Correspondingly the rates are first order in initiator. Only when the styrene concentration is appreciably less than that of the initiator does a suggestion of a fall off in rates occur. When the initiator is in excess, the position of maximum absorption of polystyryllithium is at 325 nm rather than at the normal 333 nm position. A similar downfield shift has been observed in cyclohexane for the 1:1 adduct with *n*-butyllithium.[12] Under these conditions, very little propagation occurs and complete initiation is attained with a two- to threefold excess of styrene. Under the conditions used for polymer preparation, the initiation rate will be unchanged but the propagation step will be much more competitive due to the much higher monomer concentration. Broader molecular weight distributions than obtained with *sec*-butyllithium would be expected. The technique of adding a small excess of styrene to the initiator and allowing it to react completely before adding the major portion of monomer should be particularly effective because of the different reaction orders in monomer in the two steps. These points are confirmed in Figure 3 where the results of the two types of operation are shown and compared with straightforward addition of the whole amount of monomer to *sec*-butyllithium.

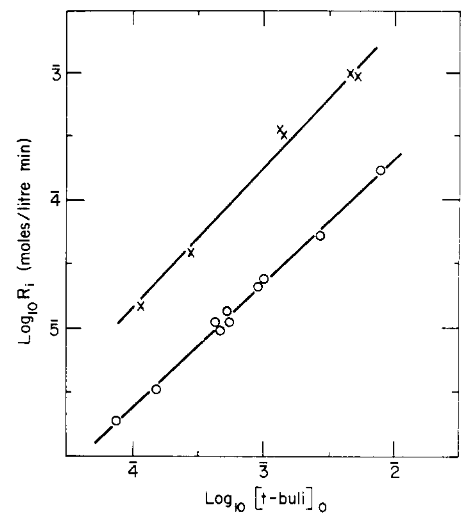

Figure 4. Dependence of initiation rate in benzene on initiator concentration at high monomer concentration: (×) isoprene, [M] > 5 × 10^{-2} *M;* (○) styrene, [M] varied between 10^{-4} and 10^{-2} *M.*

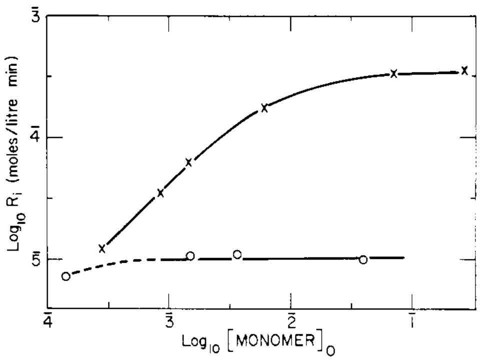

Figure 5. Effect of monomer concentration on initiation rate in benzene: (×) isoprene, [*t*-BuLi] = 1.37 × 10^{-3} *M;* (○) styrene, [*t*-BuLi] = 4.5 × 10^{-4} *M.*

Discussion

In aliphatic hydrocarbon solvents *tert*- and *sec*-butyllithium initiate polymerization of styrene and isoprene in a very similar manner. It seems reasonable to suppose that the very low initial rates observed for *tert*-butyllithium are caused by a low reactivity of the tetramers (even lower than for *sec*-butyllithium). The reaction rate increases as mixed aggregates are formed. It is known[5] that mixing of the aggregates of polyisoprenyllithium and *tert*-butyllithium does occur with reasonable rapidity although there is not as complete mixing as with *sec*-butyllithium and some *tert*-butyllithium tetramers do remain in solution. This does not seem to affect the overall reaction process. The only marked differences occur with styrene where rates decrease more rapidly after 50% conversion. It is possible that this is connected with more incomplete mixing of the aggregates, and increased importance of the competing propagation step.

In benzene, the results show larger differences between the tertiary isomer and the others than in hexane and cyclohexane. The existence of a maximum rate of initiation at high monomer concentrations and a given initiator concentration has not been observed previously. This does not prove that the phenomenon does not exist with the other isomers of butyl lithium but merely that if it does occur it is not in the concentration range where initial rates can be measured accurately. This problem already arises with *tert*-butyllithium and isoprene for the maximum rates are only reached at isoprene concentrations such that the initial rate of consumption of initiator is ~25% $\min^{-1}$. For this reason the highest rates shown in Figure 5 may be somewhat inaccurate although internal pseudo-first-order plots which are linear over a rather longer time interval were used to check the estimates of initial rates. No such problem exists with styrene and *tert*-butyllithium for the rates are first order in initiator and zero order in monomer at quite low reaction rates. The observed first-order rate constant at 30°, 0.09 $\min^{-1}$ (1.5×10^{-3} $\sec^{-1}$) (per tetramer), is close to the rate constant for intermolecular exchange found by Brown[4] and associated with the tetramer dissociation rate. This was found to be 0.5×10^{-3} $\sec^{-1}$ in toluene at 20°. (The rate constants reported in ref 4 should be multiplied by 2.3 (T. L. Brown, private communication).) We may safely assume that it would be a factor of 2 to 3 higher at 30° ($E_{\text{act}} \sim$ 10–20 kcal/mol) and some differences in rate could occur between toluene and benzene. It is tempting to assume, therefore, that the limiting rate in the reaction of *tert*-butyllithium with styrene in benzene is determined by the rate of dissociation of tetramers. This is a logical extension of the dissociation mechanism previously suggested to occur in benzene,[2] but where the primary dissociation step is slow and/or the reactivity of dissociated species is higher. It would not be possible to distinguish between reaction with the dimeric or monomeric *tert*-butyllithium since a fast reaction of styrene with either would lead to the tetramer dissociation step being rate determining. Previously only the monomeric form has been considered to be active.

A problem remains in this interpretation, namely that at high monomer concentrations isoprene reacts approximately ten times faster (k ~ 1.8×10^{-2} $\sec^{-1}$) with *tert*-butyllithium and hence considerably above the estimated rate of tetramer dissociation. A possible solution to this problem lies in the mechanism of dissociation suggested by Brown[3,4] which involves an intermediate caged species

$$(\mathrm{BuLi})_4 \rightleftarrows \{(\mathrm{BuLi})_2(\mathrm{BuLi})_2\} \rightleftarrows 2(\mathrm{BuLi})_2$$

The exchange rate (and hence presumably the styrene initiation rate) is determined by the overall rate. A higher isoprene initiation rate could be produced by interaction at the caged species step. In fact the suggestion has already been made that dienes may be more effective than aromatic solvents in solvation of the intermediate state.[4] If this is so, however, it is not clear why this type of attack does not occur in cyclohexane leading to kinetics which are zero order in monomer.

Such mechanisms can give plausible explanations for the zero order in monomer region but obviously cannot exclude other possible schemes. What is certain is that at this point the monomer does not participate in the rate-determining step. An obvious alternative mechanism involves the formation of tetramer–monomer complexes whose decomposition rates determine the observed rates. It seems unlikely that such a scheme could lead to kinetics which are first order in monomer and fractional order in initiator under the conditions of very low monomer concentration.

At lower monomer concentrations with *tert*-butyllithium in benzene the reaction characteristics change to those observed more generally with *sec*- and *n*-butyllithium as is clear from the case of isoprene. For styrene the monomer concentrations required would be extremely low and so this region was not investigated. The substituted derivative, 1,1-diphenylethylene, has been studied with an excess of initiator apparently at monomer concentrations ~5×10^{-5} *M*.[7] The fractional rate of reaction of tetramers seems to have been <2×10^{-5} $\sec^{-1}$ at 33° well below the maximum rates observed in the present study. The reaction was close to one-fourth order in initiator and first order in monomer with a rate constant of 2.8×10^{-3} $\mathrm{l.}^{1/4}$ $\mathrm{mol}^{-1/4}$ $\sec^{-1}$. The present results for isoprene under the same reaction conditions give a rate constant of 5.0×10^{-3} $\mathrm{l.}^{1/4}$ $\mathrm{mol}^{-1/4}$ $\sec^{-1}$ at 30°. In the latter case it is of interest to compare this result with that for *sec*-butyllithium in benzene where the rate constant was found to be 4.0×10^{-3} $\mathrm{l.}^{1/4}$ $\mathrm{mol}^{-1/4}$ $\sec^{-1}$.[2] (All rate constants are expressed in moles of tetramer.) The rate constants are surprisingly close and at first sight unexpected if a dissociation to a reactive monomeric butyllithium determines the reaction path. The lower rate of dissociation of *tert*-butyllithium tetramers might be expected to produce an appreciably lower equilibrium concentration of *tert*-butyllithium monomer as the reassociation steps are probably fast and diffusion controlled. The situation is, however, rather complex as the dissociation constants of both tetramer and dimer of the lithium alkyl are involved in the previously suggested dissociative mechanism. The apparent rate constant is given by $k_{\mathrm{i}}K_2^{1/2}K_1^{1/4}[\mathrm{BuLi}_4]^{1/4}$ where K_1 and K_2 are the tetramer and dimer dissociation constants and k_{i} the real rate constant for the reaction between monomeric butyllithium and an olefin. We do not know the relative values of K_2 and in addition it is at least plausible that k_{i} could be greater for *tert*-butyllithium than for *sec*-butyllithium. Note also that since K_1 appears as a one-quarter power, the overall rates are not unduly sensitive to moderate changes in this parameter.

Acknowledgment. We would like to thank Dr. D. J. Worsfold for some of the primary data shown in Figure 2, which were used in previous publications (ref 2 and 13).

References and Notes

(1) H. L. Hsieh, *J. Polym. Sci., Part A*, **3**, 163 (1965).
(2) S. Bywater and D. J. Worsfold, *J. Organometal. Chem.*, **10**, 1 (1967).
(3) T. L. Brown, *Acc. Chem. Res.*, **1**, 23 (1968).
(4) M. Y. Darensbourg, B. Y. Kimura, G. E. Hartwell, and T. L. Brown, *J. Am. Chem. Soc.*, **92**, 1236 (1970).
(5) F. Schué and S. Bywater, *Macromolecules*, **2**, 458 (1969).
(6) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **38**, 1891 (1960).
(7) R. A. H. Cassling, A. G. Evans, and N. H. Rees, *J. Chem. Soc. B*, 519 (1966).
(8) D. J. Worsfold and S. Bywater, *Can. J. Chem.*, **42**, 2884 (1964).
(9) J. E. L. Roovers and S. Bywater, *Macromolecules*, **1**, 328 (1968).
(10) C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 1807 (1960).
(11) J. E. L. Roovers and S. Bywater, *Trans. Faraday Soc.*, **62**, 1876 (1966).
(12) E. Walckiers and M. Van Beylen, Macromolecular Preprints 1199, I.U.P.A.C., Boston, 1971.
(13) A. F. Johnson and D. J. Worsfold, *J. Polym. Sci.*, **3**, 449 (1965).