A reduced moment of inertia for the O–H group equal to $1.31 \times 10^{-40}$ g. cm.$^2$ was used in the calculations.[17] With the help of standard tables,[30] the revised entropies of each isomer were calculated. The mole fractions of the two isomers were calculated from $\Delta E_0^\circ = 2.0$ kcal./mole, the partition functions for the isomers being assumed equal for this calculation. Finally, an entropy of mixing was calculated and included with the contributions from each isomer. The resulting molar entropies for acetic acid monomer are: 69.7 e.u. at 298.15°K. and 83.4 e.u. at 572.3°K. These are to be compared with the experimental values, $69.4 \pm 1.0$ and 66.9 e.u. at 298.15°K. and $85.0 \pm 2.2$ e.u. at 572.3°K.

The proposed alterations in the vibrational assignment for acetic acid monomer are clearly speculative and are intended only to indicate the type of change which is needed to remove discrepancies. The new treatment does at least yield entropies which represent a compromise between values presently available. A complete set of thermodynamic functions based on this revision is given in Table V. In obtaining each function, the contributions from the *cis* and *trans* isomers have been combined. Entropies (and free energies) of mixing have been included, $\Delta E_0^\circ$ has been added to $H^\circ - E_0^\circ$ (and $F^\circ - E_0^\circ$) for the *trans* isomer to take account of the different energy zeros, and $C_p^\circ$ includes the contribution from the change in the mole fractions of isomers with temperature.[31] In addition to these functions, the heat of formation of acetic acid monomer is needed for practical calculations. This value can be calculated from data given in Table III and the references to that table along with $(H^\circ - E_0^\circ)/T$ from Table

(30) G. N. Lewis and M. Randall, revised by K. S. Pitzer and L. Brewer, "Thermodynamics," 2nd Ed., McGraw–Hill Book Co., Inc., New York, N. Y., 1961.

(31) J. G. Aston and J. J. Fritz, "Thermodynamics and Statistical Thermodynamics," John Wiley and Sons, Inc., New York, N. Y., 1959, pp. 394–396.

V. The resulting heat of formation is $-103.1$ kcal./mole at 298.15°K., which becomes $-100.1$ kcal./mole at 0°K.

TABLE V

THERMODYNAMIC FUNCTIONS FOR ACETIC ACID MONOMER (CAL./°K. MOLE)

| $T$, °K. | $S^\circ$ | $(H^\circ - E_0^\circ)/T$ | $-(F^\circ - E_0^\circ)/T$ | $C_p^\circ$ |
|---|---|---|---|---|
| 298.15 | 69.7 | 12.0 | 57.7 | 16.8 |
| 300 | 69.8 | 12.0 | 57.8 | 16.9 |
| 400 | 75.2 | 13.7 | 61.5 | 20.4 |
| 500 | 80.1 | 15.4 | 64.7 | 23.5 |
| 600 | 84.6 | 16.9 | 67.7 | 25.9 |
| 700 | 88.8 | 18.3 | 70.5 | 27.9 |

$\Delta H_f^\circ = -100.1$ kcal./mole at 0°K.

A comparison of $C_p^\circ$ from Table V with the experimental heat capacity[5] can now be made to test further the plausibility of the revised thermodynamic functions. The most stringent comparison which can be made is at the highest temperature of the heat capacity measurements, 540.0°K., where the contribution from the monomer is greatest and the contribution from the $\Delta H$ of the monomer–dimer reaction is smallest. When the value of $C_p^\circ$ (24.4 cal./°K. mole) at 540.0°K., interpolated from Table V, is used with Taylor's results[5,10a] for the monomer–dimer equilibrium, the calculated value is 26.2 cal./°K. mole, compared with the experimental value of 25.7 cal./°K. mole. Thus the thermodynamic functions of Table V are in fair agreement with all the experimentally determined thermodynamic properties of acetic acid which are presently available.

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# The Mechanism of the Anionic Polymerization of Methyl Methacrylate. III. Effects of Solvents upon Stereoregularity and Rates in Fluorenyllithium-Initiated Polymerizations[1]

BY DONALD L. GLUSKER, RICHARD A. GALLUCCIO, AND ROGER A. EVANS

Rates of fluorenyllithium-initiated polymerizations of methyl methacrylate have been measured at $-60°$ in toluene–tetrahydrofuran mixtures containing from 0.1 to 15% tetrahydrofuran by volume and in toluene–diethyl ether mixtures containing from 2 to 20% diethyl ether by volume. The rate of disappearance of monomer under all conditions was kinetically first order, though the slope of plots of $-\ln M/M_0$ vs. time depended upon monomer concentration in some cases. In all cases, the first-order plots had a finite intercept at zero time, indicating essentially instantaneous formation of the pseudo-terminated low molecular weight polymer first described in paper II of this series.[4] Polymers prepared in toluene–diethyl ether mixtures were highly isotactic, while in toluene–tetrahydrofuran mixtures the polymers were isotactic at low tetrahydrofuran concentrations and syndiotactic at the higher concentrations. In the intermediate range of tetrahydrofuran concentrations, stereoblock polymers were obtained. A kinetic scheme is presented which serves to rationalize the dependence of the rate of polymerization upon initiator concentration and solvent composition. It is assumed that the steady-state concentration of active chains and the configurations of the polymer are a reflection of equilibria between monomer and solvent in the complex about the lithium at the chain end. On the other hand, the molecular weight distribution is assumed to be kinetically determined. Data on the dependence of gel melting point upon molecular weight of low molecular weight fractions indicate that a change in conformation of the polymer chains occurs when the chain length reaches 8–10 monomer units. This conformational change is believed to be responsible for the decrease in probability for pseudo-termination which must occur at this point.

## Introduction

The great importance of association, dissociation, and exchange equilibria of the organometallic species which are responsible for both initiation and propagation in homogeneous anionic polymerization is uni-

versally recognized. The exact features of the reactions differ appreciably in the polymerizations of different monomers and are strongly affected by solvent composition. In the polymerization of styrene by $n$-butyllithium in hydrocarbon solvents, the initiator exists as hexameric aggregates and the rate of initiation is slow with respect to that of propagation; thus, over a considerable range of the polymerization, there is

residual butyllithium present.[2] This is in distinct contrast to the polymerization of methyl methacrylate initiated by fluorenyllithium, in which under all conditions studied, fluorenyllithium has disappeared within 5 sec. of the initiation of the reaction. The previous papers in this series[3,4] presented data which demonstrated that in the polymerization of methyl methacrylate by fluorenyllithium, initiation occurs by rapid addition of the organometallic across the double bond of the monomer leaving the fluorenyl group chemically attached to the polymer chain. Radioactive tracer experiments had shown that essentially no irreversible termination occurs under the conditions used. A kinetic scheme derived as a consequence of these results involved consideration of only initiation and propagation processes. From this, it was predicted that the polymer would have a narrow molecular weight distribution, but this prediction was not borne out. Fractionation of the polymeric product indicated a very broad molecular weight distribution with a large mole fraction of polymer chains of quite low molecular weight. Experiments with radioactive terminators showed that the latter did not result from irreversible termination reactions, but from a pseudo-termination reaction which prevented them from growing to high polymer, though they retained an organometallic chain end. Kinetic measurements in 90% toluene–10% diethyl ether gave linear first-order plots of conversion vs. time, but these plots could be extrapolated to a finite intercept at zero time. This intercept corresponded to an almost instantaneous consumption of three moles of monomer per mole of initiator. These data were interpreted to explain the formation of pseudo-terminated low molecular weight fractions by a cyclization to form a complex which was reluctant to polymerize further. This cyclic complex could involve the last three monomer units on a chain of any length, but the lowest member of the series is the trimer. Plots of number average molecular weight of the polymer vs. time converged to the same intercept regardless of the ratio of initial concentrations of monomer to initiator, and that intercept was the molecular weight of the trimeric species.

The mechanism derived from these and other data had the following essential postulates: (1) chains of different steric configurations may propagate at different rates even in a homogeneous medium; (2) a high percentage of the total number of chains started undergoes a pseudo-termination whose probability is a function of the configurations of the last three monomer units in the chain; and (3) when a chain attains a minimum length of eight to ten monomer units, the probability that further additions will take place in isotactic sequence is greatly increased and the probability for pseudo-termination is greatly decreased.

The data presented in this paper show that the most salient points of our earlier work, i.e., the pseudo-termination reaction and the great decrease in its probability when the chain has reached a given minimum length, persist over a wide range of experimental conditions. Although certain adjustments are required in the detailed mechanism as a result of the greater complexity of our new data, the broad outlines of the mechanism are given further support by our recent results.

In the interim between the publication of our earlier work and the present paper, two studies of the kinetics of the anionic polymerization of methyl methacrylate

have appeared.[5,6] Both used n-butyllithium as an initiator in pure toluene. Neither of these groups was consistently successful in obtaining interpretable results, perhaps because of the problem of side reactions involving attack of butyllithium on the carbonyl group of the monomer. The kinetic data in the Russian work[5] are not given in sufficient detail to allow critical analysis. However, the kinetic equations used to analyze their data correspond to those which we described in paper II for the case where the rate of initiation is much slower than that of propagation.[4] Our own quantitative data in this regard for fluorenyllithium apply only to systems containing at least 0.1% by volume of polar solvent. In all cases, the rate of disappearance of fluorenyllithium was very rapid. It seems likely that butyllithium, which is a much stronger base than fluorenyllithium, would react at least as fast. The work of Wiles and Bywater[6] revealed a number of complexities in kinetic behavior sufficient to prevent a quantitative treatment of their data. However, the qualitative agreement between their results and our own is good enough to furnish independent support for some of the features of our mechanism. Thus, Wiles and Bywater report the presence of an appreciable amount of hexane-soluble low molecular weight polymer in all of their experiments. In the final stages of each of their reactions, a steady state is reached in which the concentration of active chains remains constant. Furthermore, they demonstrated lack of termination of these active chains by the addition of further portions of monomer which polymerized at an unchanged rate. Their kinetic curves also show the finite intercept at zero time which is such a constant feature of our own results; however, the complexities in the shape of conversion vs. time plots prevented them from ascribing any special significance to these intercepts.

## Experimental

Procedures for purification of solvents, inert atmospheres, preparation of initiator, experimental apparatus for radioactivity determinations and kinetic measurements, isolation of polymer, purification, and characterization were as described in papers I[3] and II.[4]

Tetrahydrofuran (du Pont) was dried over calcium hydride for a minimum of 24 hr., then transferred to a flask containing lithium aluminum hydride where it was stored under helium atmosphere for at least 3 days. Tetrahydrofuran was then distilled from the lithium aluminum hydride in a packed column under helium in order to effect complete removal of peroxides. The distillate was passed through Woelm neutral alumina, activity grade 1, at a ratio of 500 ml. of tetrahydrofuran to 100 g. of alumina, to remove any residual hydroquinone. It was stored over calcium hydride under helium atmosphere after vacuum degassing.

Fluorenyllithium in tetrahydrofuran was prepared in the same fashion as that described previously for solutions in diethyl ether. The resultant solution was a clear, red-orange color as opposed to the yellow color of fluorenyllithium in diethyl ether. If trace impurities were allowed to contaminate the solution, it immediately turned to a murky brown color. This appeared to be a very sensitive indication of purity; therefore, discolored solutions were discarded.

Column chromatography was carried out on columns containing 2:1 mixtures of silicic acid and Celite 545 using linear solvent gradient elution from benzene to methyl ethyl ketone for the isotactic and the syndiotactic samples and from ethylene dichloride to methyl ethyl ketone for the stereoblock sample and the mixture of isotactic with syndiotactic polymer. Ethylene dichloride was used in the latter cases since a stereoblock polymer or a mixture of isotactic and syndiotactic polymers form an insoluble gel in benzene.

Gel melting points were determined as described by Watanabe, et al.[7]

(2) D. J. Worsfold and S. Bywater, Can. J. Chem., **36**, 1891 (1960).

(3) D. L. Glusker, E. Stiles, and B. Yoncoskie, J. Polymer Sci., **49**, 297 (1961).

(4) D. L. Glusker, I. Lysloff, and E. Stiles, ibid., **49**, 315 (1961).

(5) A. Korotkov, S. P. Mitsengendler, and V. N. Krasulina, ibid., **53**, 217 (1961).

(6) D. M. Wiles and S. Bywater, Polymer, **3**, 175 (1962).

(7) W. H. Watanabe, C. F. Ryan, P. C. Fleischer, Jr., and B. S. Garrett, J. Phys. Chem., **65**, 896 (1961).

Nuclear magnetic resonance spectra were determined on a Varian HR-60 high resolution spectrometer using 10% solutions of polymer in chloroform. Spectra were measured at room temperature with tetramethylsilane as an internal standard. Instrumental conditions were chosen such that peak area ratios for the $OCH_3$, $\alpha$-$CH_3$, and $CH_2$ protons were the appropriate $3:3:2$. The three incompletely resolved peaks due to the $\alpha$-methyl groups were separated by constructing a symmetrical peak shape for the largest peak and then determining the areas of the subsidiary peaks by analytical subtraction. The sums of the peak areas thus separated corresponded to the total area under the original peak to within $\pm 3\%$.

Kinetic data were determined gravimetrically as previously described. The gravimetric results were corrected for residual lithium salts and were subjected to least squares analysis on a Bendix G-15 computer. In each case, the data were also plotted graphically to examine them for any systematic deviation from first-order kinetics.

## Results

Rates of polymerization have been measured at $-60°$ in solvent mixtures containing toluene and from 2 to 20% diethyl ether by volume or 0.1 to 15% tetrahydrofuran by volume. Fluorenyllithium concentrations were varied from 0.0009 to 0.02 mole/1.; monomer concentrations ranged from 0.078 to 0.624 mole/1. Polymers prepared in toluene–diethyl ether mixtures, regardless of concentration of ether, are isotactic and have broad molecular weight distributions. Polymers prepared in toluene–tetrahydrofuran mixtures range from predominantly syndiotactic with relatively narrow molecular weight distributions to highly isotactic with broad molecular weight distributions depending upon tetrahydrofuran concentration. In the tetrahydrofuran series, tacticity measurements were made by infrared $J$-value[8] and by nuclear magnetic resonance spectra,[9] and a relative ranking of regular sequence lengths in the polymers was achieved by gel melting point measurements.[7] Infrared $J$-values were measured for representative samples in the ether series. Since there was very little change in tacticity as a function of ether concentration, n.m.r. measurements were made for only one sample.

**Kinetics.**—Regardless of the initial conditions of the reaction or of the tacticity of the polymer being made, the kinetics of the polymerizations described in this paper possess two remarkably constant characteristics. First, plots of $-\ln M/M_0$, where $M$ is monomer concentration at time $t$ and $M_0$ is initial monomer concentration, vs. time remain linear to conversions of greater than 90%; and, second, extrapolation of these linear plots to zero time invariably leads to a finite intercept. Even in a few experiments in pure toluene, which we do not report in detail here because of lack of reproducibility in the rate constants, the reaction was kinetically first order to excellent precision. A first-order plot which is linear to high conversion demands that the reaction satisfy the expression

$$-d \ln M/dt = k[X] = \text{constant}$$

where $X$ = active chain ends; that is, the concentration of active chain ends is constant throughout the reaction once a steady state is established. The number average molecular weight of the high polymer isolated from any of these polymerization reactions showed that only a small fraction of the initiator molecules in the reaction mixture actually formed active chain ends. The sequence of events occurring over the first few monomer additions fixes this concentration of active chains for the remainder of the reaction, but we have no data which serve to elucidate the exact dependence of the steady-state concentration of active chains upon initial conditions.

(8) W. E. Goode, F. H. Owens, R. P. Fellmann, W. H. Snyder, and J. E. Moore, *J. Polymer Sci.*, **46**, 317 (1960).

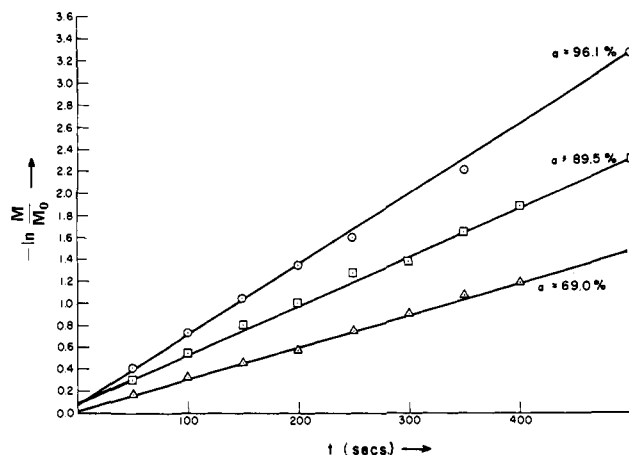(9) F. A. Bovey and G. V. D. Tiers, *ibid.*, **44**, 173 (1960).



Fig. 1.—First-order plots for polymerizations in 90% toluene–10% tetrahydrofuran; percentage conversion, $\alpha$, is given for the last point in each run; $[M_0]$ = 0.312 mole/1. for all runs. Fluorenyllithium concentrations were: ⊙, 0.009 mole/1.; ▢, 0.005 mole/1.; △, 0.002 mole/1.

The finite conversion intercept on all kinetic plots including those for reactions which lead to syndiotactic polymers indicates that the events described in the second paper of this series which lead to pseudo-terminated low molecular weight polymers occur for syndiotactic as well as isotactic polymers. For isotactic polymers, the intercept remains relatively constant and indicates an essentially instantaneous conversion of three monomer units/initiator unit. For reactions at higher concentrations of tetrahydrofuran, where highly syndiotactic polymers are formed, the conversion intercept is not constant. This is the result of an increase in the propagation rate until it has become of the same order of magnitude as the initiation rate. We demonstrated this by isotope dilution experiments similar to those described in paper I.[3] The reaction was terminated after 5 sec. by the addition of radioactive acetic acid. The products generated during this very short interval were then analyzed, with the emphasis upon those which might have arisen from residual fluorenyllithium. In 10% tetrahydrofuran–90% toluene, these experiments indicated the presence of polymer having molecular weight as high as 3000, formed within the first 5 sec. of reaction. In diethyl ether–toluene systems and at low concentrations of tetrahydrofuran, only the trimer can be found within the first 5 sec. Under all conditions, over 99% of the fluorenyllithium has disappeared in this period of time.

In Fig. 1 a set of typical first-order plots are reproduced to indicate the degree of experimental correspondence to first-order kinetics and the variation of the conversion intercept in tetrahydrofuran–toluene systems. The column labeled $k_p$ in Tables I and IV represents an apparent first-order rate constant which is the slope of the first-order plots.

In Table I are compiled all of the kinetic data and in Tables II and III, the structural characterizations for polymers prepared in toluene–tetrahydrofuran mixtures. In Tables IV and V are compiled similar data for polymers prepared in toluene–diethyl ether systems.

The slope of the first-order plots depends upon the half-power of the initiator concentration at all tetrahydrofuran concentrations. In diethyl ether–toluene mixtures, the slope depends upon the first power of initiator concentrations at the higher ether concentrations but increases to greater orders in initiator as the ether concentration is lowered. Figure 2 is a plot of $\log k_p/(FlLi)_0^{1/2}$ vs. log tetrahydrofuran concentration at constant monomer concentration. At the low con-

TABLE I

RATE DATA FOR FLUORENYLLITHIUM-INITIATED POLYMERIZATION OF METHYL METHACRYLATE IN TOLUENE–TETRAHYDROFURAN MIXTURES AT −60°

| Run | % THF by vol. | [THF], moles/l. | [MMA]$_0$, moles/l. | [FlLi]$_0$, moles/l. | $k_p \times 10^3$, sec.$^{-1}$ | $\dfrac{k_p \times 10^2}{[\text{FlLi}]_0^{1/2}}$ | $\dfrac{k_p \times 10^2}{[\text{FlLi}]_0^{1/2}[\text{MMA}]_0^{1/3}}$ | $\dfrac{k_p \times 10^2}{[\text{FlLi}]_0^{1/2}[\text{MMA}]_0^{-1}}$ |
|---|---|---|---|---|---|---|---|---|
| 1 | 15.0 | 1.839 | 0.312 | 0.0040 | 7.33 | 11.58 | .. | .. |
| 2 | 15.0 | 1.839 | .312 | .0010 | 3.82 | 12.01 | .. | .. |
| 3 | 10.0 | 1.227 | .312 | .0090 | 6.08 | 6.40 | 9.44 | .. |
| 4 | 10.0 | 1.227 | .312 | .0050 | 4.35 | 6.16 | 9.09 | .. |
| 5 | 10.0 | 1.227 | .312 | .0020 | 2.78 | 6.23 | 9.19 | .. |
| 6 | 10.0 | 1.227 | .156 | .0050 | 3.54 | .. | 9.29 | .. |
| 7 | 10.0 | 1.227 | .078 | .0050 | 2.70 | .. | 8.95 | .. |
| 8 | 7.5 | 0.920 | .312 | .0090 | 3.12 | 3.29 | .. | .. |
| 9 | 7.5 | .920 | .312 | .0070 | 2.84 | 3.40 | .. | .. |
| 10 | 5.0 | .613 | .312 | .0070 | 2.42 | 2.89 | .. | .. |
| 11 | 5.0 | .613 | .312 | .0017 | 1.14 | 2.77 | .. | .. |
| 12 | 2.5 | .306 | .312 | .0071 | 1.58 | 1.88 | .. | .. |
| 13 | 2.5 | .306 | .312 | .0010 | 0.531 | 1.68 | .. | .. |
| 14 | 1.0 | .123 | .312 | .0095 | 1.59 | 1.63 | .. | .. |
| 15 | 1.0 | .123 | .312 | .0009 | 0.448 | 1.50 | .. | .. |
| 16 | 0.1 | .012 | .312 | .0020 | .248 | 0.554 | .. | 1.73 |
| 17 | .1 | .012 | .312 | .0049 | .352 | 0.503 | .. | 1.57 |
| 18 | .1 | .012 | .156 | .0076 | 1.19 | .. | .. | 2.12 |
| 19 | .1 | .012 | .078 | .0071 | 1.89 | .. | .. | 1.75 |

TABLE II

STRUCTURAL DATA ON HIGH POLYMER FRACTIONS ISOLATED FROM THE RUNS LISTED IN TABLE I

| Run | [THF], % by vol. | $\overline{M}_n$ | $\overline{M}_v$ | $\overline{M}_v/\overline{M}_n$ | α term$^a$ | $J$-value | G.m.p.$^b$ vs. type II, °C. | G.m.p.$^b$ vs. type I, °C. | G.m.p.$^b$ alone, °C. |
|---|---|---|---|---|---|---|---|---|---|
| 1 | 15.0 | 16,650 | 39,800 | 2.38 | ~100 | 117 | 85.4 | .. | .... |
| 2 | 15.0 | 44,500 | 358,000 | 8.05 | ~100 | ... | .. | .. | .... |
| 3 | 10.0 | .... | .... | .. | ... | ... | .. | .. | .... |
| 4 | 10.0 | 16,049 | 33,900 | 2.12 | 100 | 106 | 85.3 | .. | .... |
| 5 | 10.0 | 42,150 | 126,000 | 2.99 | 100 | 110 | 86.1 | .. | .... |
| 6 | 10.0 | 8,930 | 14,800 | 1.66 | 100 | ... | .. | .. | .... |
| 7 | 10.0 | 4,100 | .... | .. | 100 | ... | .. | .. | .... |
| 8 | 7.5 | 8,800 | 13,800 | 1.57 | 100 | 94 | 80.1 | .. | .... |
| 9 | 7.5 | 10,000 | 15,460 | 1.53 | 100 | 102 | 82.5 | .. | .... |
| 10 | 5.0 | 12,100 | 38,240 | 3.16 | 100 | 87 | 79.9 | .. | .... |
| 11 | 5.0 | 26,600 | 258,500 | 9.72 | ~48 | 82 | 82.5 | .. | .... |
| 12 | 2.5 | 10,600 | 40,500 | 3.82 | ~80 | 58 | 60.6 | .. | Betw. −20 and −78 |
| 13 | 2.5 | 43,900 | 139,470 | 3.18 | 84.6 | 51 | 71.5 | 55.1 | 70 |
| 14 | 1.0 | 12,900 | 51,560 | 4.00 | 100 | 41 | <−20 | 57.1 | <−20 |
| 15 | 1.0 | 41,400 | 192,400 | 4.64 | 81.2 | 45 | 40.8 | .. | 55 |
| 16 | 0.1 | 33,850 | 410,700 | 12.1 | 61 | 33 | <−20 | .. | .... |
| 17 | .1 | 30,400 | 371,700 | 12.2 | 73.8 | 36 | <−20 | 76.5 | No gel |
| 18 | .1 | 13,300 | ..... | .. | 98.8 | ... | .. | .. | .... |
| 19 | .1 | 11,100 | ..... | .. | 100 | ... | .. | .. | .... |
| s | 5% Et$_2$O | 15,020 | 218,860 | 14.6 | 100 | 35 | .. | .. | .... |

$^a$ After withdrawal of a sufficient number of aliquots for kinetics, the remainder of the reaction mixture was generally allowed to polymerize for approximately 1 hr. α term represents the percentage conversion when the reaction was terminated. The molecular weights listed are for polymers isolated by precipitation at that time. For calculation of percentage of chains as high polymer, these numbers were adjusted to 100% conversion, by assuming linear increase in $\overline{M}_n$ with conversion. $^b$ G.m.p. = gel melting point; type I = syndiotactic standard, type II = isotactic standard.

TABLE III

N.M.R. DATA ON HIGH POLYMER FRACTIONS ISOLATED FROM THE RUNS LISTED IN TABLE I

| Run | [THF], % by vol. | s | h | i | μ[1] | μ[s] | p[I] | ρ |
|---|---|---|---|---|---|---|---|---|
| 1 | 15.0 | 0.806 | 0.125 | 0.069 | 2 | 14 | 0.13 | 1.7 |
| 4 | 10.0 | .834 | 091 | .075 | 2.7 | 20 | .12 | 2.4 |
| 9 | 7.5 | .66 | .17 | .17 | 3 | 9 | .26 | 2.2 |
| 11 | 5.0 | .692 | .067 | .241 | 8 | 21 | .27 | 3.3 |
| 12 | 2.5 | .39 | .153 | .457 | 7 | 6.2 | .53 | 3.3 |
| 14 | 1.0 | .196 | .115 | .689 | 13 | 4.3 | .75 | 3.0 |
| 15 | 1.0 | .222 | .098 | .680 | 15 | 5.4 | .73 | 3.9 |
| 16 | 0.1 | .105 | .145 | .750 | 11 | 2.4 | .82 | 1.9 |
| s | 5% Et$_2$O | .074 | .044 | .882 | 40 | 4.4 | .90 | 4 |

centration end, the data fit reasonably well to a line having a slope of 0.45. At the high concentration, the data fit a slope of 1.9. Thus, at low concentrations of tetrahydrofuran, where the polymer produced is isotactic, the dependence upon tetrahydrofuran concentration is close to half order; at high concentrations of tetrahydrofuran, when the configuration of the polymer produced has become syndiotactic, the rate dependence upon tetrahydrofuran is approximately second order.

Monomer concentration was changed in solvent mixtures containing 10% diethyl ether, and in those with 0.1 or 10% tetrahydrofuran. The best fit to the data is given by an order in monomer of $^1/_3$ at 10% tetrahydrofuran and −1 at 0.1%, whereas, in the case of diethyl ether, no effect upon $k_p$ was observed. Thus, for the systems examined, only in 10% diethyl ether does the reaction appear to be truly first order in monomer as evidenced by the independence of the slopes of first-order plots upon monomer concentration.

## TABLE IV
### RATE DATA FOR FLUORENYLLITHIUM-INITIATED POLYMERIZATION OF METHYL METHACRYLATE IN DIETHYL ETHER–TOLUENE MIXTURES AT −60°

| Run | % Et₂O by vol. | [Et₂O]₀, moles/l. | [MMA]₀, moles/l. | [FlLi]₀, moles/l. | $k_p \times 10^4$, sec.$^{-1}$ | $\dfrac{k_p \times 10^2}{[FlLi]_0}$ | $\dfrac{k_p}{[FlLi]_0^{1/2}}$ | $\dfrac{k_p}{[FlLi]_0^2}$ |
|---|---|---|---|---|---|---|---|---|
| a | 20.0 | 1.926 | 0.312 | 0.0200 | 7.39 | 3.69 | .. | ... |
| b | 20.0 | 1.926 | .312 | .0100 | 3.36 | 3.36 | .. | ... |
| c | 20.0 | 1.926 | .312 | .0100 | 5.50 | 5.50 | .. | ... |
| d | 20.0 | 1.926 | .312 | .0050 | 1.88 | 3.76 | .. | ... |
| e | 20.0 | 1.926 | .312 | .0025 | 1.53 | 6.12 | .. | ... |
| f | 10.0 | 0.963 | .312 | .0200 | 8.36 | 4.18 | .. | ... |
| g | 10.0 | .963 | .312 | .0150 | 7.39 | 4.93 | .. | ... |
| h | 10.0 | .963 | .312 | .0100 | 5.05 | 5.05 | .. | ... |
| i | 10.0 | .963 | .312 | .0100 | 4.94 | 4.94 | .. | ... |
| j | 10.0 | .963 | .624 | .0100 | 5.30 | 5.30 | .. | ... |
| k | 10.0 | .963 | .156 | .0100 | 5.47 | 5.47 | .. | ... |
| l | 10.0 | .963 | .078 | .0100 | 5.54 | 5.54 | .. | ... |
| m | 10.0 | .963 | .312 | .0075 | 3.97 | 5.29 | .. | ... |
| n | 10.0 | .963 | .312 | .0050 | 1.93 | 3.86 | .. | ... |
| o | 10.0 | .963 | .312 | .0025 | 1.16 | 4.67 | .. | ... |
| p | 7.5 | .722 | .312 | .0100 | 4.73 | 4.73 | .. | ... |
| q | 7.5 | .722 | .312 | .0100 | 5.38 | 5.38 | .. | ... |
| r | 5.0 | .481 | .312 | .0175 | 31.79 | 18.16 | 1.37 | ... |
| s | 5.0 | .481 | .312 | .0108 | 13.24 | 12.30 | 1.18 | ... |
| t | 5.0 | .481 | .312 | .0025 | 1.43 | 5.72 | 1.14 | ... |
| u | 2.0 | .193 | .312 | .0157 | 46.72 | 32.96 | .. | 18.83 |
| v | 2.0 | .193 | .312 | .0128 | 16.45 | 12.81 | .. | 9.96 |
| w | 2.0 | .193 | .312 | .0077 | 10.66 | 13.84 | .. | 18.03 |
| x | 2.0 | .193 | .312 | .0058 | 6.42 | 10.95 | .. | 18.69 |
| y | 2.0 | .193 | .312 | .0043 | 1.88 | 4.37 | .. | 10.17 |
| z | 2.0 | .193 | .312 | .0025 | 0.68 | 2.72 | .. | 10.88 |

## TABLE V
### STRUCTURAL DATA ON HIGH POLYMER FRACTIONS ISOLATED FROM THE RUNS LISTED IN TABLE IV

| Run | % Et₂O by vol. | $\overline{M}_n$ | $\overline{M}_v$ | $\overline{M}_v/\overline{M}_n$ | α term[a] | J-value |
|---|---|---|---|---|---|---|
| a | 20.0 | 7,930 | 86,940 | 11.0 | 95.0 | .. |
| b | 20.0 | 13,700 | 108,000 | 7.9 | 100.0 | .. |
| c | 20.0 | 14,590 | ..... | .. | 100.0 | .. |
| d | 20.0 | 18,413 | 141,000 | 7.7 | 54.8 | 37 |
| e | 20.0 | 24,792 | 160,470 | 6.4 | 46.9 | .. |
| f | 10.0 | 13,671 | 190,290 | 13.9 | 95.9 | .. |
| g | 10.0 | 13,600 | 220,000 | 16.2 | 100.0 | .. |
| h | 10.0 | 16,600 | ..... | .. | 100.0 | .. |
| i | 10.0 | 19,520 | 249,400 | 12.8 | 84.5 | .. |
| j | 10.0 | 22,600 | 226,000 | 10.0 | 97.1 | .. |
| k | 10.0 | .... | ..... | .. | 88.8 | .. |
| l | 10.0 | .... | ..... | .. | 91.3 | .. |
| m | 10.0 | 20,900 | 286,930 | 13.7 | 78.5 | 36 |
| n | 10.0 | 24,680 | 350,500 | 14.2 | 54.8 | .. |
| o | 10.0 | 34,390 | 433,350 | 12.6 | 40.9 | .. |
| p | 7.5 | .... | ..... | .. | ... | .. |
| q | 7.5 | .... | ..... | .. | ... | .. |
| r | 5.0 | 12,436 | 218,860 | 17.6 | 100.0 | 39 |
| s | 5.0 | 15,016 | 218,860 | 14.6 | 100.0 | 35[b] |
| t | 5.0 | 28,000 | 433,000 | 15.5 | 43.8 | 37 |
| u | 2.0 | 10,035 | 108,880 | 10.8 | 100.0 | 40 |
| v | 2.0 | 16,892 | 178,210 | 10.5 | 100.0 | .. |
| w | 2.0 | 20,134 | 427,660 | 21.2 | 100.0 | 35 |
| x | 2.0 | 21,229 | 348,860 | 16.4 | 90.3 | 32 |
| y | 2.0 | 21,769 | 429.930 | 19.7 | 52.9 | 33 |
| z | 2.0 | 23,462 | 319,100 | 13.6 | 24.5 | 38 |

[a] See footnote a, Table II.  [b] N.m.r. data on polymer from run s were s = 7.4%, h = 4.4%, i = 88.2%.

Data at 2% diethyl ether concentration were appreciably less reproducible than any of the others listed. However, it should be re-emphasized that even in this case the first-order plots of the experimental data were excellently linear to high conversions, and it is only irreproducibility in the initial establishment of the steady-state concentration of active chain ends which

is responsible for the irreproducibility in $k_p$ observed. The same comment applies to the strange orders in monomer in the tetrahydrofuran–toluene mixtures described above. In every case, the first-order plots describe the experimental data faithfully. It is the slope of the first-order plot which depends so strangely upon the initial conditions of the reaction.
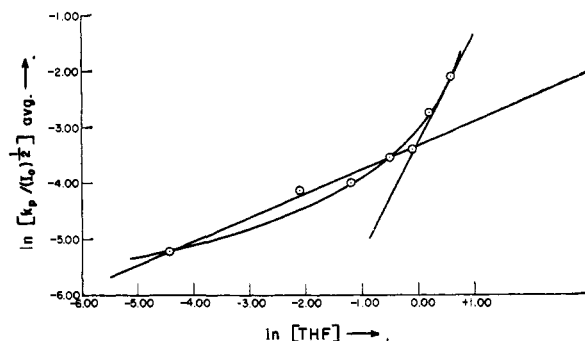


Figure 2.

**Characterization of Polymer Structure.**—We feel that the physical parameters used to characterize the stereoregularity of poly-(methyl methacrylate) may be ranked in order of increasing ability to distinguish between polymers of equal average tacticity in terms of the average length of regular stereosequences. The infrared J-value is presumed to measure solely the average number of isotactic or syndiotactic placements in the polymer chain with no indication of the stereosequence lengths or their distribution. Thus a stereoblock polymer, a mixture of isotactic and syndiotactic polymers, or a truly atactic material could have the same infrared J-value. The n.m.r. spectra allow analysis to proceed one step further by assignment of quantitative values to triads of isotactic, $i$, syndiotactic, $s$, and heterotactic, $h$, configurations. The n.m.r. spectra may be used[9] to determine whether a single probability for isotactic or syndiotactic addition

describes the set of configurational triads obtained. More complicated analyses such as those of Miller[10] or of Coleman and Fox[11,12] may also be applied to n.m.r. data to give an estimate of average stereosequence length.

The n.m.r. data giving the fraction of $s$, $h$, and $i$ triads in a polymer have been manipulated by Coleman and Fox to calculate:

$p[\mathrm{I}]$ = the probability that a placement selected at random is isotactic
   $= i + (h/2)$
$\mu[\mathrm{I}]$ = the number average length of closed isotactic sequences
   $= (2i + h)/h$
$\mu[\mathrm{s}]$ = the number average length of closed syndiotactic sequences
   $= (2s + h)/h$
$\rho$ = the persistence ratio, a measure of the deviation of sequence distributions from those predicted by random statistics
   $= \mu[\mathrm{I}] \cdot p[\mathrm{s}] = \left(\dfrac{2i + h}{h}\right)\left(s + \dfrac{h}{2}\right)$

Values of these parameters for our polymers are given in Table III. The value of $p[\mathrm{I}]$ represents the average isotacticity of the polymer and may be seen to increase steadily as tetrahydrofuran concentration is decreased. For a stereoblock polymer, both $\mu[\mathrm{I}]$ and $\mu[\mathrm{s}]$ will have large values; these tend to occur at 1, 2.5, and 5% tetrahydrofuran concentrations. The value of $\rho$, the persistence ratio, also reaches its highest levels for the tetrahydrofuran-containing systems in this concentration range.

**Gel Melting Point.**—The gel melting point, which is unique to poly-(methyl methacrylate), has been described by Watanabe, et al.[7] When dilute solutions of isotactic and of syndiotactic poly-(methyl methacrylate) in a number of specific solvents (in the present work, dimethylformamide) are mixed, a gel rapidly forms; this gel has a sharp reproducible melting point. Data have been presented to indicate that the melting points of the gels formed from mixtures of a standard isotactic sample and a series of syndiotactic samples are a function of the relative lengths of the syndiotactic sequences in the series.[7] By examining the gel melting point behavior of some fractions of hexane-soluble very low molecular weight polymers, we have been able to establish semiquantitatively the limits of the sequence length required for gel formation. In Table VI, we list the gel melting points for a series of low molecular weight fractions isolated from a polymerization in tetrahydrofuran–toluene in which the hexane-insoluble polymer was highly syndiotactic, and from a polymerization in diethyl ether–toluene in which the hexane-insoluble polymer was highly isotactic.

The gels of the polymers from the diethyl ether–toluene system were formed by mixing with a high molecular weight syndiotactic polymer while those for the polymers isolated from tetrahydrofuran–toluene mixtures were formed by mixing with a high molecular weight isotactic polymer. The gels melt at gradually decreasing temperatures as the number average molecular weight becomes smaller. When the molecular weight is decreased below a certain minimum value, a precipitous drop in the gel melting point occurs. This very sharp drop in gel melting point could be interpreted to mean that polymers below a certain molecular weight are more atactic than are those above that molecular weight, or that a certain number of isotactic or syndiotactic placements in sequence are required to allow a molecular conformation which can

(10) R. L. Miller, *S.P.E. Trans.*, **3**, 123 (1963).
(11) B. D. Coleman and T. G. Fox, *J. Chem. Phys.*, **38**, 1065 (1963).
(12) Preprints, International Symposium of Macromolecular Chemistry, Paris, July, 1963.

TABLE VI

GEL MELTING POINTS OF LOW MOLECULAR WEIGHT FRACTIONS

I. From polymerization in 90% toluene–10% tetrahydrofuran; high molecular weight polymer is syndiotactic

| $\bar{M}_n$ | G.m.p. (°C.) vs. high mol. wt. isotactic p(MMA) |
|---|---|
| 3700 | 79.2 |
| 2500 | 78.8 |
| 2000 | 77.4 |
| 1400 | 74.2 |
| 900 | $\sim -20$ |

II. From polymerization in 90% toluene–10% diethyl ether; high molecular weight polymer is isotactic

| $\bar{M}_n$ | G.m.p. (°C.) vs. high mol. wt. syndiotactic p(MMA) |
|---|---|
| 19,700 | 94.7 |
| 8,380 | 85.9 |
| 2,530 | 80.0 |
| 1,120 | 75.0 |
| 968 | 57.5[a] |
| 711 | $< -78$ |

[a] Two samples obtained from Dr. F. Owens served to define further these limits. They were prepared with $H^3$-labeled phenylmagnesium bromide in toluene and isolated by column chromatography; $\bar{M}_n$'s were determined by measurement of specific activity. A fraction with $\bar{M}_n = 928$ formed a gel which melted at 57.3°, while one with $\bar{M}_n = 880$ formed no gel down to −78°.

contribute to gel formation. We were unfortunately unable to determine $J$-values and n.m.r. spectra on the specific samples reported in Table VI. However, infrared and n.m.r. measurements were made on a series of low molecular weight fractions prepared under analogous conditions. There is some ambiguity in using these parameters for such low molecular weight substances, since it is not clear whether the differences in infrared and n.m.r. spectra among the various stereoisomers of high molecular weight poly-(methyl methacrylate) persist at very low molecular weights. These spectral differences may be directly related to the configurational differences among the chains, or may result from preferred conformations which are influenced by the configurational differences. If the latter is the case, these molecular conformations may not persist at very low molecular weights. Within the considerable uncertainty raised by this point, the infrared and n.m.r. data for low molecular weight fractions indicate that there may be little change in stereospecificity for low molecular weight isotactic samples in the molecular weight region below that which will contribute to gel formation. Materials isolated from polymerizations in which high polymer is highly isotactic are themselves apparently highly isotactic. On the other hand, materials isolated from polymerizations in which the high polymer is syndiotactic are apparently more nearly heterotactic. The gel melting point data on the low molecular weight fractions imply that a regular sequence length of about ten units is necessary to establish conformations which can contribute to gel formation with a high molecular weight partner. The effect of increasing sequence length beyond this minimum is to increase gradually the gel melting point. The effect of molecular weight in general, however, is much smaller than that of change in sequence length. The gel melting point remains constant for $\bar{M}_n \geq 19,000$ for this type of polymer. We should also note that a stereoblock polymer will gel by itself in dimethylformamide. Observation of the direction of change of the gel melting point of the stereoblock polymer upon addition of increments of either isotactic or syndiotactic standards gives a qualitative estimate of which type
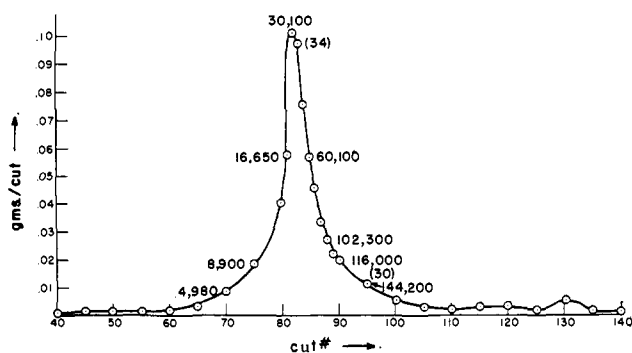
Fig. 3.—Chromatographic fractionation of isotactic polymer. Numbers next to points are $\bar{M}_n$ values; $\bar{M}_n$ of whole polymer = 15,000, $J$ = 35.
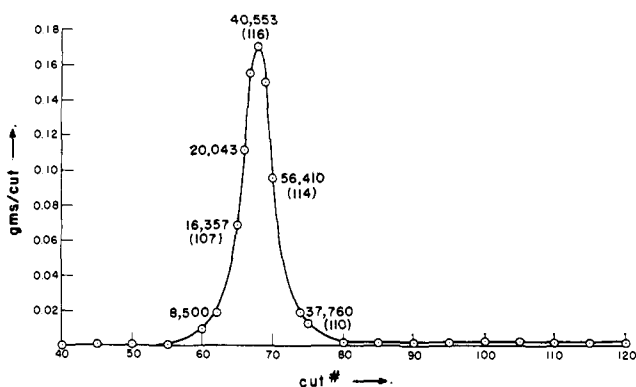


Fig. 4.—Chromatographic fractionation of syndiotactic polymer. Numbers next to points are $\bar{M}_n$ values, numbers in parentheses are infrared $J$-values; $\bar{M}_n$ of. whole polymer = 16,650, $J$ = 117.

of stereoregular sequence is the longer in the original stereoblock sample.

The gel melting point and the n.m.r. data given in Tables II and III for samples made at 1 and at 2.5% tetrahydrofuran concentrations indicate that they are stereoblock polymers. They gel when mixed with either isotactic or syndiotactic standards, and the higher molecular weight samples gel by themselves. Both $\mu$[I] and $\mu$[s] are relatively large for these samples. An interesting comparison may be made between the two samples prepared at 1% tetrahydrofuran for which n.m.r. data are almost identical. The large differences in gel melting point alone or $vs.$ the standard isotactic polymer seem to be greater than could be accounted for by the fourfold difference in molecular weight and probably indicate that the higher molecular weight sample has some appreciably longer regular sequences; $\mu$[I] and $\mu$[s] are very similar for these two polymers, but the persistence ratio, $\rho$, is greater for the high molecular weight sample, 3.9 $vs.$ 3.0, and thus may also reflect the presence of some longer sequences, even though the average lengths are the same.

Another indication of the relative abilities of infrared, n.m.r., and gel melting point determinations to describe regular sequence lengths is given by a comparison of data from run 11, Tables II and III, with those for a sample prepared by free radical initiation at 210°. The $J$-value of the free radical sample is 78, which is very close to that of the anionic sample. On the other hand, the gel melting point of the free radical sample is only 37.1°, and the n.m.r. data for the free radical sample show $s$ = 45%, $h$ = 41%, $i$ = 14%,[13] which give $\mu$[I] = 1.7, $\mu$[s] = 3.2, $\rho$ = 1.1.

The striking similarity in gelation behavior of a

(13) R. K. Graham, D. L. Dunkelberger, and J. R. Panchak. $J. Polymer Sci.$, **59**, 543 (1962).
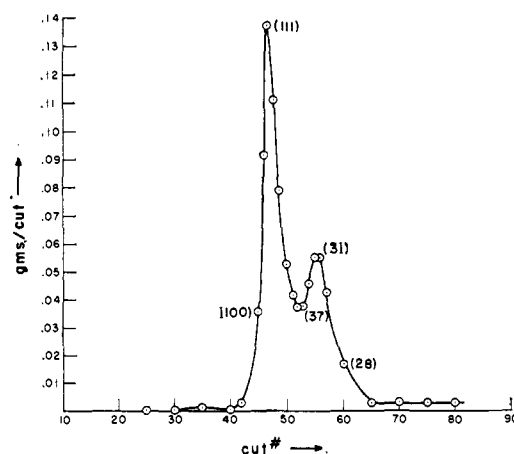


Fig. 5.—Chromatographic fractionation of a 1:1 by weight mixture of isotactic and syndiotactic polymer. Numbers next to points are infrared $J$-values.
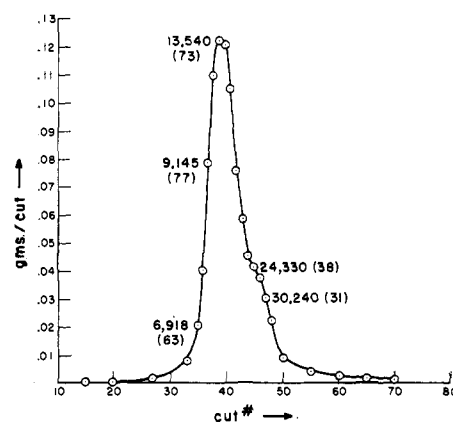


Fig. 6.—Chromatographic fractionation of a stereoblock polymer. Numbers next to points are $\bar{M}_n$ values, numbers in parentheses are infrared $J$-values; $\bar{M}_n$ of whole polymer = 10,600, $J$ = 58.

stereoblock polymer to that of a mixture of isotactic and syndiotactic polymers is reflected in many other physical properties. Indeed, the only previously published evidence which serves to establish samples of stereoblock polymers as chemical entities rather than mixtures of separate chains of isotactic and syndiotactic polymers are the competitive hydrolysis experiments of Glavis.[14] To resolve this question with respect to the present series of polymers, chromatographic fractionations were performed on an isotactic polymer from 5% diethyl ether, a syndiotactic polymer from 15% tetrahydrofuran, a mixture of these, and on a stereoblock polymer from 2.5% tetrahydrofuran. The data are given in Fig. 3, 4, 5, and 6. They show clean separation for the mixture, whereas the stereoblock polymer gives a single peak having intermediate $J$-value, with a small shoulder of predominantly isotactic material. There is no evidence of a high $J$-value syndiotactic polymer in this sample. Thus these polymerizations occur under conditions which favor primarily stereoblock polymerization rather than independent polymerizations of chains of different tacticities. However, the existence of a small amount of isotactic material in the block polymer does indicate that it may be possible under some conditions to obtain such independent polymerizations of chains with different tacticities.

### Discussion

Propagation reactions which show nonintegral dependence upon initiator concentrations in homogeneous

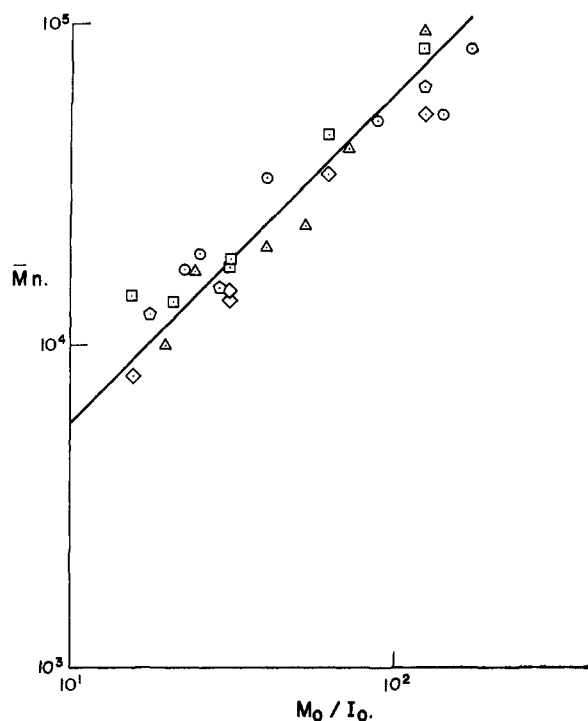(14) F. J. Glavis, $ibid.$, **36**, 547 (1959).

Fig. 7.—$\bar{M}_n$ vs. [$M_0$]/[$I_0$] for polymerizations run in toluene–diethyl ether mixtures. Diethyl ether concentrations by vol. were: ⊙, 0%; △, 2%; ⊘, 5%; ▢, 10%; ◇, 20%.



Fig. 8.—$\bar{M}_n$ vs. [$M_0$]/[$I_0$] for polymerizations run in toluene–tetrahydrofuran mixtures. Tetrahydrofuran concentrations by vol. were: ◁, 0.1%; ◯, 1%; ▢, 2.5%; ▽, 5%; △, 7.5%; ◇, 10%; ◨, 15%.

anionic polymerization are by now a familiar phenomenon, with the publication of many examples from the polymerization of styrene and diene hydrocarbons. With hydrocarbon monomers, half-order dependence upon initiator changes to first order in polar solvents.[15,16] This has been interpreted to indicate the presence of dimeric aggregates of the active chain ends which may dissociate into much more reactive monomeric species. The dissociation is enhanced by increasing solvent polarity. A further complication in the polymerization of styrene by $n$-butyllithium in tetrahydrofuran–toluene mixtures was discovered by Bywater and Worsfold.[16] They have shown the existence of complexes between polystyryllithium and tetrahydrofuran which may contain either one or two molecules of tetrahydrofuran per lithium. The complex containing one tetrahydrofuran per lithium is a highly reactive one, whereas that containing two molecules of tetrahydrofuran per lithium is much less reactive. Therefore, the dependence of the rate of propagation upon tetrahydrofuran concentration goes through a maximum with increasing tetrahydrofuran.

The data on anionic polymerization of methyl methacrylate presented in this paper may also be interpreted in terms of a number of rapid equilibria between different complex organometallic species, each of which is capable of reacting with monomer at its own characteristic rate. However, there are differences in detail which are to be attributed to differences in the ability of the monomers to coordinate lithium and in particular to compete with polar solvents at coordinating lithium. The exact nature of the counterion and of the species which fill its coordination sphere is all important in determining both the stereospecificity of the reaction and its kinetics.

For methyl methacrylate polymerization, we must introduce a further refinement since a large percentage of the total number of chains initiated do not partici-
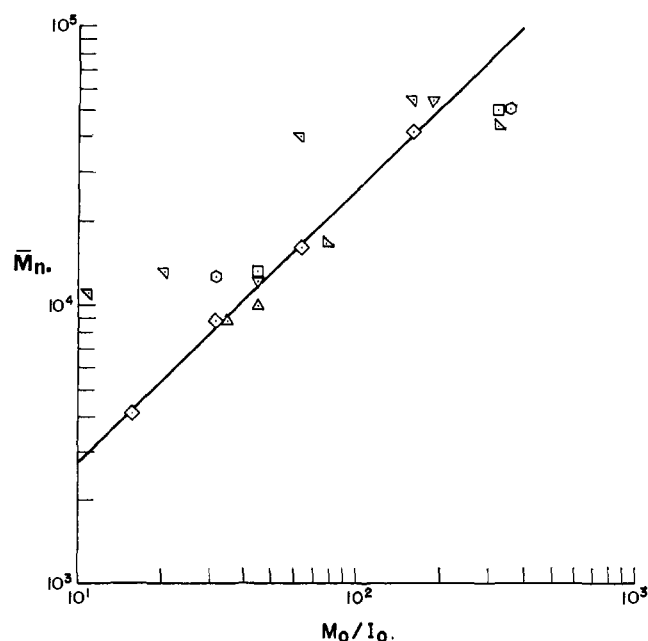
(15) M. Morton, E. E. Bostick, and R. Livigni, Rubber and Plastics Age, 42, 397 (1962).
(16) S. Bywater and D. J. Worsfold, Can. J. Chem., 40, 1564 (1962).

pate in the propagation reactions once the steady state is reached. What we have previously designated as pseudo-terminated and active chains served to distinguish between those low molecular weight polymeric species containing carbon–lithium bonds reactive toward acetic acid but not toward monomer, and the smaller number of chains which retain their activity in propagation. In the light of the complex kinetics described in the present work, we have further subdivided "active" chains into a large pool of relatively inactive states in rapid reversible equilibria with a much smaller concentration of highly reactive states through which the actual propagation reaction proceeds. With respect to molecular weight distributions or stereoregular sequence distributions, this subdivision of the active chains is immaterial, as long as all have a high probability of being in a propagating state a large number of times during the reaction.

In order to simplify our attempt to treat the kinetic data with respect to dependence upon initiator and Lewis base concentration, we assume that the fraction of active vis-à-vis pseudo-terminated chains is constant for all initial conditions. Since initiation has been shown to be extremely rapid, we are treating here the steady-state condition after all of the events of the first 8 to 10 monomer additions, which establish pseudo-terminated chains, have already taken place. The validity of the approximation that active chain concentration is a constant fraction of fluorenyllithium concentration may be checked by comparing number average molecular weights for the hexane-insoluble fractions as a function of initial monomer to initiator ratios for the various toluene–Lewis base mixtures. Figure 7 gives these data for polymers isolated from reactions in diethyl ether–toluene mixtures ranging from 2 to 20% diethyl ether. It can be seen that the data fall on a rough straight line which has a slope of 1.02. From these data, it would appear that 17.6% of the initiator leads to high polymer for all ether runs. Figure 8 is a similar plot for the tetrahydrofuran data. The data for 0.1% tetrahydrofuran concentration lie above the line; and, in fact, the data for these isotactic samples fall in line with the other isotactic polymers
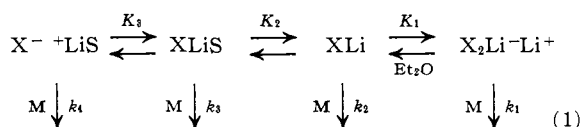
made in diethyl ether. Three other points from runs at very high monomer to initiator ratio, greater than 300, fall well below the line. Since the rates of these runs were in line with all the others, too much of the hexane-soluble fraction may have been carried along during isolation of these polymers by repeated solution and precipitation. From the line drawn through the other points one may estimate that 34.2% of the chains appear as high polymer. Within the very broad limits imposed by the precipitation method of separating high from low molecular weight polymer, the percentage of chains capable of growing to high polymer remains fairly constant within a given Lewis base–toluene mixture over a considerable range of concentration.

Since isotactic polymerizations in 10% diethyl ether or in 0.1% tetrahydrofuran appear to have the same percentage of active chains, even though the rates of the reactions follow different kinetic laws, we conclude that the steady-state concentration of active chains is determined by initial rapid reactions which do not decisively influence the over-all rates of polymerization. A quantitative description of these initial reactions would require data from the first few seconds of the reaction. Since our apparatus was unsuitable for obtaining such data, we are at present unable to determine exactly what factors fix the number of active chains during the establishment of the steady state. A kinetic scheme consistent with our data and with the preceding arguments follows:

We let XLi stand for an active polymer chain, and $[XLi] = n[FlLi]_0$, where $n$ is a fractional constant and $[FlLi]_0$ is the initial concentration of fluorenyllithium; S is a strong enough Lewis base to induce some ion pair formation, e.g., tetrahydrofuran, but not diethyl ether; M is monomer.

$$X^- {}^+LiS \underset{}{\overset{K_3}{\rightleftarrows}} XLiS \underset{}{\overset{K_2}{\rightleftarrows}} XLi \underset{Et_2O}{\overset{K_1}{\rightleftarrows}} X_2Li^-Li^+$$

$$M \downarrow k_4 \qquad M \downarrow k_3 \qquad M \downarrow k_2 \qquad M \downarrow k_1 \qquad (1)$$

$-d \ln M/dt =$

$$(k_1K_1[XLi] + k_2 + k_3K_2[S])[XLi] + k_4\sqrt{K_3K_2[S][XLi]}$$

where

$K_1 = [X_2Li^-Li^+]/[XLi]^2$; $K_2 = [XLiS]/[XLi][S]$; $K_3 = [X^-][LiS^+]/[XLiS]$

Diethyl ether was not given an explicit role in $K_1$ for reasons which will be discussed below. For diethyl ether–toluene media, we assume that $k_3K_2[S] \ll k_1K_1[XLi] + k_2$, thus
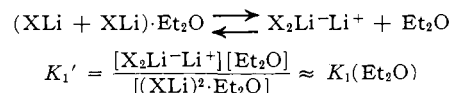
$$-d \ln M/dt = (k_1K_1[XLi] + k_2)[XLi] \qquad (2)$$

Equation 2 predicts a second-order dependence of rate upon initiator when $k_1K_1 \gg k_2$. A plot of $-d \ln M/dt \cdot [XLi]^{-1}$ vs. $[XLi]$ should be a straight line with slope $k_1K_1$ and intercept $k_2$. Table VII gives rate constants derived from such plots. These values should be taken to indicate only order of magnitude since so many assumptions were involved in their derivation. Reasonable straight lines were obtained for data at all ether concentrations except the lowest, 0.193 $M$, where there was considerable scatter in the kinetic data.

### TABLE VII
#### RATE CONSTANTS FOR TOLUENE–ETHER MIXTURES

| [Et$_2$O]. moles/l. | $k_1K_1$ | $k_2$ | $k_1K_1$[Et$_2$O] |
|---|---|---|---|
| 0.963 | $\sim$0 | $5 \times 10^{-2}$ | ... |
| .481 | $8.2 \times 10^{-2}$ | $3.9 \times 10^{-2}$ | $3.9 \times 10^{-2}$ |
| .193 | $21.0 \times 10^{-2}$ | $\sim$0 | $4.0 \times 10^{-2}$ |

The last column in Table VII implies that $K_1$, the formation constant for dimeric species, decreases

linearly with increasing ether concentration. It is difficult to formulate an equilibrium to correspond with this, but it might have the form

$$(XLi + XLi)\cdot Et_2O \underset{}{\overset{}{\rightleftarrows}} X_2Li^-Li^+ + Et_2O$$

$$K_1' = \frac{[X_2Li^-Li^+][Et_2O]}{[(XLi)^2\cdot Et_2O]} \approx K_1(Et_2O)$$

To explain half-power dependence upon [XLi] in tetrahydrofuran, we must assume that $K_1 \approx 0$, $K_2 \gg K_3$, and $k_4 \gg k_3$, i.e., $(k_2 + k_3K_2[S])[XLi] \ll k_4 \cdot \sqrt{K_3K_2[S][XLi]}$. Then

$$-d \ln M/dt \approx k_4\sqrt{K_3K_2[S][XLi]} \qquad (3)$$

Since the rate dependence remains half order at even the lowest tetrahydrofuran concentrations, we cannot separate these constants. In eq. 3, the concentration of tetrahydrofuran appears under the square root sign. Thus, the half-order dependence upon tetrahydrofuran concentration observed at low concentrations of tetrahydrofuran where propagation is predominantly isotactic implies that there is one tetrahydrofuran molecule per active lithium chain end, while at the high tetrahydrofuran concentrations where rate dependence is second order and propagation is predominantly syndiotactic there are four tetrahydrofurans per active chain end. Hence, the distribution of ligands about lithium may include at least one tetrahydrofuran molecule and still allow isotactic propagation, although the introduction of this single tetrahydrofuran in the complex is sufficient to alter the kinetics of the reaction drastically. Since we obtain stereoblock polymers rather than random ones in the intermediate regions, the rate of interchange of ligands about lithium must be appreciably slower than the propagation rate. If there were an appreciable difference in propagation rates for chain ends having differing distributions of ligands about lithium, the interchange reactions must take place sufficiently often during the course of the polymerization so that we observe only an average rate. Alternate explanations would include very few interchanges and identical rates for differing chain end complexes, or few interchanges and constant concentration of each type of chain end complex.

We have no quantitative interpretation of the dependence of the slope of the first-order plot upon $[M]^{1/3}$ in 10% tetrahydrofuran and upon $[M]^{-1}$ in 0.1% tetrahydrofuran. It is probable that these orders are the result of competition between monomer and tetrahydrofuran for complexing of lithium on the chain end, with tetrahydrofuran slightly stronger at complexing. At 10% tetrahydrofuran concentration, where the order in monomer is positive, the number average molecular weight of the hexane-insoluble fraction is proportional to the monomer-to-initiator ratio whether the monomer or the initiator be altered. This implies a strictly constant concentration of active chains, with monomer to tetrahydrofuran ratio perhaps influencing the value of $k_3$ or that of $k_4$. On the other hand, in 0.1% tetrahydrofuran, a reduction in monomer concentration does not lead to a corresponding reduction in number average molecular weight; rather, there is an apparent decrease in percentage of active chains with decreasing monomer. Thus, the percentage of active chains appears to depend upon monomer concentration as well as tetrahydrofuran concentration, while the negative dependence of the rate upon monomer concentration implies that increasing monomer concentration tends to decrease $K_3$, hence the concentration of $X^-$ $^+LiS$.

The molecular weight distribution of the hexane-insoluble material as indicated by viscosity to number

average molecular weight ratios generally gets narrower as the tetrahydrofuran concentration is increased. At tetrahydrofuran concentrations above 5%, $M_v/M_n$ also depends upon the monomer to initiator ratio in the polymerization, getting larger as $M_0/I_0$ increases. Under certain initial conditions, we obtain syndiotactic polymers of very broad molecular weight distribution; thus one may prepare polymers having broad molecular weight distributions which are either isotactic or syndiotactic (though we have observed narrow distribution polymers only for highly syndiotactic polymers prepared at the higher ranges of tetrahydrofuran concentration). Also, the configurations of the polymers are independent of the kinetics of the polymerizations. We suggest that configurational sequences in anionic polymerization of methyl methacrylate do not result from rate-determining processes, but are influenced by equilibria whose dependence upon initial conditions of the reaction is different from that of the rates of the reaction and in turn the molecular weight distributions.

Only one basic change in the mechanism put forth in paper II of this series is required by our present results. That is abandonment of the hypothesis that differences in the equilibrium constants for cyclization are the predominant result of differences in configuration of the last three units at the end of a polymer chain. We now find that pseudo-termination reactions of low molecular weight polymers occur during both syndiotactic and isotactic propagations. Steady state kinetics for all polymerizations indicate that the probability of pseudo-termination must decrease after the initial stages of the reaction. The gel melting point results with the low molecular weight fractions seem to indicate that both isotactic and syndiotactic polymers may undergo a change in conformation at a degree of polymerization of 8 to 10 monomer units. The conformation which the active chain assumes at 8 to 10 monomer units may indeed be helical but there is no direct evidence from this work to support this. The major unsettled point left by the present work is the lack of explanation of how initial conditions affect the equilibrium constants for cyclization to a pseudo-terminated state.

In order to explain broad molecular weight distributions, it still remains necessary to postulate that there is a finite probability for the rapidly propagating active chains to revert to pseudo-terminated ones with, on the average, an equal number of pseudo-terminated chains becoming active to those which are inactivated. Coleman and Fox[17] have carried out a detailed calculation of molecular weight distributions to be expected from a mechanism having two interconvertible states of greatly differing kinetic activity. They also assume that the rates for isotactic and for syndiotactic propagation within these two states are quite different, and this assumption has enabled them to calculate probable sequence distributions as well. In order for their mechanism to predict broad molecular weight distributions for high molecular weight polymers, the rate of interconversion of the two states must be very low relative to the rates of addition of monomer. Under these circumstances, their mechanism predicts that a polymerization carried out in intermediate ranges of tetra-

hydrofuran concentration would lead to a mixture of isotactic and syndiotactic chains rather than a stereoblock polymer.

Our colleague, Dr. Sonja Krause, has independently suggested a way of treating a mechanism having two interconvertible states of greatly differing activity which represents a considerable mathematical simplification (cf. Krause, DeFonso, and Glusker[18]). She has assumed that the exchange of activity occurs by a bimolecular mechanism such that one active chain and one inactive chain interact to reverse roles. In such a circumstance, the concentration of either active or inactive chains remains constant. For any particular value of monomer to initiator ratio, this mechanism contains only two adjustable constants: (1) the fraction of active chains and (2) the ratio of the rate constant for exchange of activity, $k_t$, to that for addition of monomer, $k_p$. The first constant can vary only from 0 to 1. The monomer to initiator ratio is an experimentally determined quantity; thus this mechanism in essence has only one parameter which may vary over wide ranges. These calculations predict: (a) that the molecular weight distribution at 100% conversion may become broader as the starting monomer to initiator ratio increases (cf. data in Table II); (b) that the molecular weight distribution at 100% conversion becomes narrower as the ratio $k_t/k_p$ increases (there are no direct experimental data to bear upon this point, but the conclusion agrees with that of Fox and Coleman); (c) that the ratio $M_w/M_n$ goes through a maximum during the course of polymerization for any finite value of $k_t$; (d) that any value of $M_w/M_n$ between 1.01 and infinity is possible at the end of the polymerization depending upon the particular values of the two adjustable constants that are picked; (e) the greater the percentage of active chains for any given monomer to initiator ratio and value of $k_t/k_p$, the narrower the distribution.

No inconsistencies have been found between any of the above predictions and any of the available experimental data. Several of the predictions are susceptible to direct experimental tests. It is not immediately clear whether Coleman and Fox's exchange mechanism involving independent probabilities becomes mathematically equivalent to that which we have described when the product of their independent rate constants for exchange times the concentration of the individual species is equal for the reaction in either direction. Independent probabilities may be preferable if the mathematical treatment allows prediction of as many experimentally testable results as does the bimolecular exchange mechanism. The initial suggestion for bimolecular exchange was made on mathematical grounds, as a simple way to obtain an exactly constant fraction of active chains, and we have no evidence that bimolecular exchange actually takes place.

(17) B. D. Coleman and T. G. Fox, *J. Am. Chem. Soc.*, **85**, 1241 (1963).

(18) S. Krause, L. DeFonso, and D. L. Glusker, *J. Phys. Chem.*, paper to be submitted.