53745-75-8; syndiotactic *m*-ClSt, 107830-48-8; isotactic *m*-ClSt, 116002-24-5; syndiotactic *p*-ClSt, 62319-29-3; isotactic *p*-ClSt, 29297-96-9; syndiotactic-*p*-BrSt, 107911-22-8; $TiCl_4$, 7550-45-0; $TiBr_4$, 7789-68-6; $Ti(OCH_3)_4$, 992-92-7; $Ti(OC_2H_5)_4$, 3087-36-3; $(\eta\text{-}C_5H_5)TiCl_2$, 31781-62-1; $(\eta\text{-}C_5H_5)TiCl_3$, 1270-98-0; $(\eta\text{-}C_5(CH_3)_5)TiCl_3$, 12129-06-5; $(\eta\text{-}C_5H_5)_2TiCl_2$, 1271-19-8; $(\eta\text{-}C_5(CH_3)_5)_2TiCl_2$, 11136-36-0; $(\eta\text{-}C_5(CH_3)_5)_2TiClH$, 115912-71-5; $Ti(acac)_2Cl_2$, 17099-86-4; H_2O, 7732-18-5.

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Near Monodisperse Ethylene–Propylene Copolymers by Direct Ziegler–Natta Polymerization. Preparation, Characterization, Properties

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ABSTRACT: In Ziegler copolymerization of ethylene and propylene, appropriate premixing of aluminum alkyl and vanadium catalyst components prior to contacting with the monomers can give essentially instantaneous initiation. Transfer and termination reactions at temperatures below 40 °C are slow enough, compared to propagation, to permit very narrow molecular weight distribution (MWD) polymer (M_z:M_w:M_n ~ 1.3:1.2:1.0) to be formed in a plug flow reactor. Due to the different reactivity of the monomers, the polymer has a tapered compositional distribution. This can be shown by fractionation of the polymer prior to and after thermal degradation, with compositional analysis of the fractions. Chain lifetimes in the polymerization are of the order of seconds. The narrow MWD produces obvious changes in rheological properties as compared to EPM produced in a conventional backmixed reactor, yielding behavior typical of high plateau modulus, anionically prepared, hydrogenated polyisoprenes. In the linear viscoelastic region steady-state compliances can be measured with the product of the compliance and plateau modulus $J_e^0G_N^0 = 3.5$. The dependence of the normalized loss modulus G''/G''_{max} versus frequency is "typical" of monodisperse hydrogenated polyisoprenes and polybutadienes. This is the first report of the preparation of such "statistical" ethylene–propylene copolymers at practical polymerization temperatures, i.e. higher than −40 °C, and with both ethylene and propylene present in the initiation step.

Introduction

Ziegler–Natta polymerizations are carried out commercially on a grand scale. Billions of pounds of polyolefin plastics and elastomers are produced annually. Regardless of the polymerization process, these polymers are characterized by molecular weight distributions (MWD) as broad as or broader than the most probable, i.e. M_z:M_w:M_n ~ 3:2:1. This is a result of a number of factors including reactor residence time distribution, number of catalyst species present, and the interrelationship of initiation, propagation, termination, and transfer reactions. In the case of ethylene–propylene copolymerization all commercial producers employ backmixed reactors[1-3] which, in the case of a single catalyst species, will produce a most probable MWD, with uniform composition along the individual chain contours. For product performance improvements in selected applications it is advantageous to prepare narrow MWD versions of these polymers with varied intramolecular compositional distributions.

On the laboratory scale, Doi[4-8] and co-workers have produced narrow MWD polypropylene and poly(propylene–ethylene) propylene block copolymers at temperatures below −50 °C with a "living" Ziegler system based on vanadium acetylacetonate. Following Doi, Evens and Pijpers[9] polymerized propylene at −78 °C and also attempted to make block polymers. In the presence of ethylene both sets of workers find that the very narrow MWD's (<1.2 M_w/M_n) obtained with pure propylene tend to be broadened somewhat. These results were obtained in batch polymerizations. At low temperature, propylene sequences tend to become syndiotactic.

Junghanns et al.,[10] as part of a larger study, examined ethylene–propylene copolymerization in a tubular reactor with $VOCl_3/Et_3Al_2Cl_3$ catalyst. These studies were carried out at ambient temperature and above. Product characterization indicated that the MWD was narrower than that produced in a backmixed reactor, but no quantitative data were given. Also with use of $VOCl_3$, and in addition VCl_4, Doi and co-workers[11] were unsuccessful in attempts to prepare narrow MWD polypropylene. Their failure presumably was due to initiation or convective mixing problems.

In this paper we report on a procedure for preparing ethylene–propylene copolymers at temperatures up to 50 °C with a narrower MWD than obtained previously. To make narrow MWD polymer, initiation must be rapid compared to chain propagation and both these reactions in turn should be fast compared to termination or transfer. Furthermore the residence time distribution in the reacting medium must be that of a batch or plug flow reactor. We

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have chosen to call a reactor scheme when chain initiation and growth are separated "mix free".[12]

In anionic polymerization, i.e. BuLi-catalyzed polybutadiene, the initiation step is intrinsically fast compared to growth and there is essentially no transfer or termination. With Ziegler components this is not generally the case. In fact, initiation and growth usually overlap and there are termination and transfer reactions occurring at the same time. In the case of Doi's work,[4] by operating below −50 °C, transfer and termination are suppressed, and with vanadium tris(acetylacetonate) or similar vanadium components, initiation, including alkylation or reduction, is significantly faster than propagation for propylene polymerization.

In Junghann's et al.[10] studies it is difficult to determine the MWD obtained with the nonpremixed catalyst $VOCl_3/Et_3Al_2Cl_3$. Under the conditions specified in that work we find catalyst initiation and propagation are not well separated in time (i.e. position in the reactor) and the MWD is not significantly narrowed relative to a backmixed reactor polymerization (CFSTR).

In this paper we present the results of a study aimed at producing EPM copolymer with MWD's significantly narrower, for example, M_z:M_w:M_n = 1.3:1.2:1.0, than previously obtained above −40 °C. Such copolymers are made in a tubular reactor with a single catalyst species at conditions that give essentially instantaneous chain initiation, with chain termination and transfer adequately slow. Because of the reactivity difference between the monomers, the copolymer also contains an intramolecular compositional distribution significantly broader than for EPM's made in a CFSTR.

We have explored, and discuss in this paper, three aspects of Ziegler-catalyzed polymerization to narrow MWD copolymers. Copolymerization in a tubular reactor was modeled numerically to indicate the effect of kinetics on polymer characteristics; experimental conditions were found that produce narrow MWD polymer in accord with model predictions; and the MWD and compositional distribution were characterized. Also some commercially significant applications for these new EPM structures are indicated. We believe this to be the first demonstration of ethylene–propylene copolymerization at commercially attractive temperatures which yields narrow MWD polymers.

Experimental Section

(A) Materials. Polymerizations were carried out in polymerization grade hexane (Phillips) which is a mixture of hexanes, approximately 85% normal, with the remainder predominantely methylpentanes. Solvent was purified prior to use by passing it over silica gel (W.R. Grace Co., Davison Chemical Div., PA-400 20–40 mesh) and 4A molecular sieves (Union Carbide, Linde Div., 4A $^1/_{16}$ in. pellets) to remove polar impurities which act as catalyst poisons. Gaseous ethylene (Liquid Carbonic, Specialty Gas Div.) and propylene (Union Carbide Linde Div.) were purified by passing them over hot Cu_2O (270 °C) to remove oxygen followed by 4A molecular sieves for water removal. The polymers were deashed by vigorous contact with dilute HCl and were stabilized with 0.1% Irganox 1076, a hindered phenol (Ciba Geigy). The catalysts employed: VCl_4 (Union Carbide), $VOCl_3$ (Stauffer), and $V(acac)_3$ (Aldrich), were used as received.

Solvents used in characterization experiments were 1,2,4-trichlorobenzene (Aldrich) stabilized with 0.05 wt % Ionol (Aldrich) for chromatography and the same solvent without antioxidant for ^1H and ^{13}C NMR spectrometry. Solvent–nonsolvent fractionations were performed with reagent grade n-hexane and 2-propanol.

(B) Characterization. Molecular weight measurements were made by a combination of GPC (Waters 150C) with on line light scattering (LALLS) (KMX-6 Chromatix-Milton Roy). The instrumentation and procedures have been described.[14-16] All results are reported without correction for spreading (but see experiments below which probe that aspect). We find spreading corrections to be small, e.g. less than 0.05 on M_w/M_n. In any event, all results are presented with reference to well-characterized, readily available standards. Data were analyzed by using customized software written in conjunction with Computer Inquiry Systems, a division of Beckman Inc.

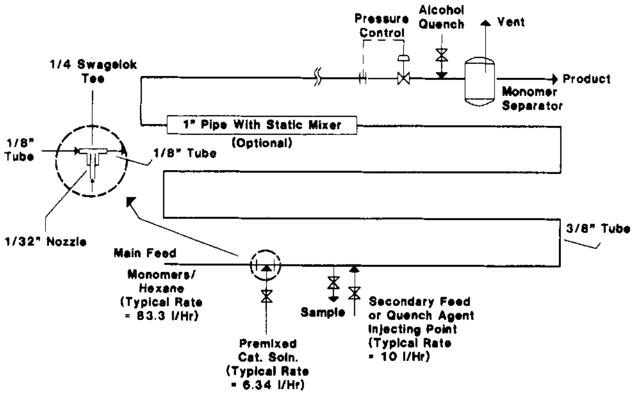


Figure 1. Configuration of tubular reactor.

We employed a value of −0.104 cm^3/g for dn/dc at 633 nm in 1,2,4-trichlorobenzene at 135 °C. This value appears to be invariant with ethylene content and is typical of results for polyethylene.[17,18] Others[19,20] have obtained values somewhat lower (e.g. −0.101). Except in viscosity comparisons made with model EP's,[21] the errors are negligible. A value of −0.104 yields a viscosity molecular weight relationship[3,21] very close to that obtained independently by Scholte et al.[22]

M_z/M_w from GPC/LALLS and M_w/M_n from elution time calibration are employed to characterize the distribution. Both of these ratios are easily perturbed by small weight fractions of either high or low MW polymer, respectively. The derivative of the integral weight fraction distribution with respect to log M, d$w(M)$/d log M, is also reported at its maximum. This quantity is 1.54 for a most probable distribution and ∞ for a Poisson. For typical high MW anionic "standards" values of up to 6.0 have been obtained on our instrument. For decane and squalane we obtain values of 16 and 10. This parameter is less subject to perturbation by distribution tails and signal/noise performance of the particular GPC. It is dependent on the resolution capability of the columns at a given molecular weight, and it must be studied as a function of column loading, however.

Bulk rheological measurements were made by using a variety of techniques including gravity driven creep,[23] Mooney viscometery, and cone and plate and plate–plate rheometry. These latter measurements were made with an original Rheometrics mechanical spectrometer and the newer Rheometrics System 4 in both oscillatory and steady-shearing modes. Correlation with results on model EP's on an absolute basis[21] was of interest, but we strove to measure viscosity, η_0, and compliances, $J_e{}^0$, in the low-frequency linear viscoelastic region, as well as G' and G'' to obtain the plateau modulus, $G_N{}^0$, so the product $J_e{}^0G_N{}^0$ could be used as a measure of MWD.

Ethylene contents were measured by using infrared analysis by ASTM procedure D3900.

Compositional distributions were evaluated by dissolution of the polymer in normal hexane, at about 1 wt %, with successive precipitation of fractions using 2-propanol. Such fractionations were carried out on polymer as recovered from the reactor and on samples that were thermally degraded as ~0.005 in. films under nitrogen at approximately 320 °C for 30 min. This reduced the polymer molecular weight to approximately 3000–5000 and with subsequent fractionation revealed the intramolecular heterogeneity of the directly polymerized molecules.

(C) Polymerization Procedures. All polymerizations reported here were carried out in an adiabatic continuous flow tubular reactor with the configuration shown in Figure 1. Monomers are dissolved in chilled hexane and brought into the reactor through an impingement mixing tee. At this point, the premixed catalyst and cocatalyst stream is mixed with the mainstream.

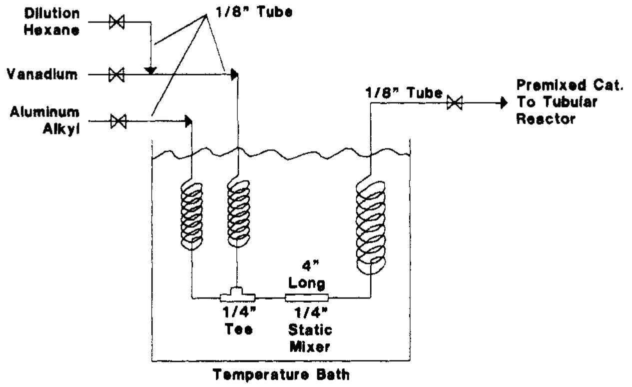


Figure 2. Vanadium catalyst and aluminum alkyl cocatalyst premixing unit.

Velocity ratios of about 3:1 (sidestream to mainstream) appear to be adequate for obtaining proper mixing. The linear velocity of the mainstream is about 200 cm/s. Before the polymer is formed the Reynolds number is typically (12–14) × 10^3. Even with monomer concentrations at only 0.1 M (ethylene), polymer grows to tens of thousands in molecular weight in less than 0.5 s so the catalyst/monomer mixing step is important in producing homogeneous product. At ethylene/propylene ratios greater than 1:1 (weight) it is very difficult to attain rapid enough mixing to completely avoid the formation of some very high ethylene content polymers and consequent intermolecular polymer heterogeneity. Furthermore, due to the poor solubility of high ethylene polymers in hexane it is important to balance hexane feed temperature, polymer concentration, monomer feed ratio, and mixing in the reactor in order to avoid mass fouling. The reactor is kept liquid filled by operating at 300 KPa and above to prevent formation of a vapor phase. The reactor effluent passes through a pressure control valve and into a monomer separator and then to recovery.

Catalyst–cocatalyst premixing is performed in a device such as that in Figure 2. Mixing is less critical here. Typical residence times are on the order of 5–10 s at 0–10 °C.

Various additional monomer or "quenching" sidestreams can be added along the reactor. The course of the polymerization was followed by taking polymer samples or quenching the polymerization at points along the reactor length. In general, adding a quench agent, e.g. 2-propanol, into the reactor was more effective in obtaining a representative sample than sampling through a line due to the additional reaction occurring during the residence time in the sample line. Samples were deashed with dilute HCl and recovered by steam stripping of the solvent followed by mill or vacuum oven drying of the product to remove residual volatiles. The product so prepared was analyzed for composition, compositional distribution, and molecular weight distribution using the techniques described. Our studies indicate no effect of the by recovery process (milling etc.) on the product MW or MWD.

Modeling of EPM Polymer Characteristics in Batch and Plug Flow Tubular Reactors

It is well-known that copolymer MWD and compositional distributions (CD) are affected by the type of polymerization reactor used. Continuous-flow-stirred reactors (CFSTR) give a narrow CD since the comonomer ratio remains constant during chain growth. On the other hand, in a batch or plug flow reactor the comonomer ratio is not constant, in general, and the CD is broad. (For purposes of discussion we shall speak primarily in terms of plug flow only, but obviously the same considerations apply to batch reactors also.)

Compositional variation can occur both between chains and along the contour of a given chain. For free radical catalyzed copolymerizations, which are characterized by slow initiation and fast propagation, batch reactors lead to a broader intermolecular than intramolecular CD. The reverse is true for anionic living copolymerizations with fast initiation. In this case all the chains will be similar in composition, but there will be a strong composition change along the length of a chain, especially if the comonomers differ substantially in activity.

MWD in a CFSTR is characterized by M_w/M_n equal to 2.0 (i.e. a "most probable" distribution) for polymerizations in which there is one type of active center and chains terminate by disproportionation, spontaneously, by transfer or not at all (i.e. only on exit from the reactor). Similarly, M_w/M_n equals 1.5 for termination by combination (i.e. random coupling of two most probable MWD's). As first shown by Denbigh,[24] the use of a batch reactor gives the same or broader MWD than a CFSTR for free radical polymerization kinetics, but a narrower MWD for living polymerizations.

Throughout this discussion it is assumed that there are no long chain-branching reactions perturbing the MWD. There is strong evidence for this from the rheological properties discussed below. This does not mean long chain branching is always absent in EP copolymers.

The foregoing discussion is limited to polymerization with a single active catalyst species. If multiple species exist, as is common for Ziegler catalysts,[13] both CD and MWD will be broad, and polymer characteristics will depend primarily on the type of catalyst used rather than the type of reactor.

The effect of the reactor type on CD and MWD is related to the ratio of chain growth time to reactor residence time. When the ratio is much smaller than one, as in free radical copolymerization, a batch or tubular reactor gives a broad intermolecular CD and an MWD the same or broader than a CFSTR. When the ratio is close to one, as it can be in living polymerizations, the CD is primarily intramolecular and a batch reactor narrows the MWD as compared to CFSTR. EPM kinetics in the −40 to +50 °C temprature range are such that chain initiation can be rapid, but termination and transfer limit chain growth. Consequently it is not immediately obvious how MWD and CD would be altered in switching from a CFSTR to a batch or tubular reactor. Morawetz[25] has shown that for homopolymerizations with fast initiation and spontaneous termination, MWD is narrower in the batch reactor than a CFSTR, in the absence of chain transfer.

Wehner's[26] calculations for EPM polymerization in a tubular reactor under laminar flow conditions also indicates a narrowed polymer MWD (M_w/M_n = 1.3). However, the empirical polymerization rate expression he used to obtain this result cannot easily be related to any polymerization mechanism.

In order to explore the nature of EP copolymer expected from a plug flow reactor, we numerically modeled copolymerization behavior by using the kinetic scheme and rate constants previously published by Cozewith[27] (see tables I and II), which were generated from data obtained in a CFSTR, as a basis for the calculations. A catalyst system that produces one active species was assumed. The absolute values of the rate constants employed here are not as important as the ratios of initiation, propagation, termination, and transfer. In particular, we wished to examine the extent of MWD narrowing that could be obtained in the presence of termination and transfer over a range of initiation rates.

Integration of the complex set of simultaneous differential equations representing the rates for the various reactions in the polymerization mechanism was avoided by modeling the reactor as 200 stirred tank stages in series.[28,29] This converts the differential equations to algebraic equations, and by adjusting the residence time per stage so that the monomer conversion does not exceed 2%/stage, an excellent approximation to the plug flow

Table I
EPM Kinetic Model[a]

reaction	kinetics	rate const	rate
chain initiatn	1. $C + M_1 \rightarrow P_1$	k_{i1}	$k_{i1}CM_1$
propagatn	2. $P_i + M_1 \rightarrow P_{i+1}$	k_{11}	$k_{11}P_iM_1$
	3. $P_i + M_2 \rightarrow Q_{i+1}$	k_{12}	$k_{12}P_iM_2$
	4. $Q_i + M_1 \rightarrow P_{i+1}$	k_{21}	$k_{21}Q_iM_1$
	5. $Q_i + M_2 \rightarrow Q_{i+1}$	k_{22}	$k_{22}Q_iM_2$
cat. deactivation	6. $P_i, Q_i \rightarrow V_i$	k_t	$k_t(P_i, Q_i)$
	7. $P_i, Q_i + M_2 \rightarrow V_i$	k_{tm}	$k_{tm}(P_i, Q_i)M_2$
chain transfer	8. $P_i, Q_i + M_2 \rightarrow V_i + Q_1$	k_{trm}	$k_{trm}(P_i, Q_i)M_2$
	9. $P_i, Q_i + A \rightarrow V_i + P_1$	k_{tra}	$k_{tra}(P_i, Q_i)A$
	10. $P_i, Q_i + H_2 \rightarrow V_i + C$	k_{trh}	$k_{trh}(P_i, Q_i)H_2$

[a] Abbreviations: C, catalyst; M_1 and M_2, ethylene and propylene, respectively; P_i, growing chain ending in ethylene; Q_i, growing chain ending in propylene; A, aluminum alkyl; H_2, hydrogen; (P_i, Q_i), sum of growing chain concentrations of either M_1 or M_2 ended chains.

Table II
EPM Rate Constants

rate const[a]	reaction	cat. V salt/$AlEt_2Cl$ (37 °C)
k_{i1}	initiation with ethylene	1.4
k_{11}	propagation	2.7×10^2
k_{12}	propagation	5.3×10
k_{22}	propagation	1.1
k_{21}	propagation	6.4×10
k_t	chain termination—spontaneous	2.7×10^{-3}
k_{tm}	chain termination—with propylene	4.2×10^{-4}
k_{trm}	chain transfer—with propylene	4.2×10^{-3}
k_{tra}[b]	chain transfer—with aluminum alkyl	2.5×10^{-4}
k_{trh}	chain transfer—with hydrogen	5.5×10

[a] mol, L, s units. [b] For transfer rate proportional to 2 (Al/V-1).

reactor can be obtained. The accuracy of the tanks-in-series model was tested by comparing it to numerical integration of the differential equations describing the homopolymerization mechanism:

$$C + M \rightarrow P_1 \quad \text{initiation}$$

$$M + P_i \rightarrow P_{i+1} \quad \text{propagation}$$

$$P_i + T \rightarrow V_i + C \quad \text{transfer}$$

$$P_i \rightarrow V_i \quad \text{termination}$$

We found that both methods calculate essentially the same monomer conversion, M_w/M_n and M_n at the exit of the reactor. However, in the tanks-in-series model, M_w/M_n is constrained to be 2.0 in the first stage when it actually is less than 2.0 at the start of polymerization. Consequently, M_w is too high initially and then gradually approaches the value from numerical integration as the reaction time increases. The extent of polymerization required before the two M_w values are in close agreement depends on the magnitude of the rate constants and the conversion increment per stage. For the rate constants given in Table II, the tanks-in-series model yields M_w within 10% of the correct value when the total monomer conversion reaches 10%, if the per stage monomer conversion is 1–2%. This is reduced to 3% total monomer conversion at 0.2–0.5% conversion per stage. Obviously the per stage conversion must be quite small if it is necessary to calculate M_w/M_n accurately at short reaction time and less than 10% monomer conversion.

As an example, plug flow tubular behavior is examined for the V salt/$AlEt_2Cl$ rate constants in Table II with reactor feed concentrations of 0.61 mol/L for ethylene, 1.0 mol/L for propylene, and 1.75×10^{-4} mol/L for the catalyst. The effect of the chain initiation rate constant on polymer concentration and M_w/M_n in the absence of chain transfer (all transfer constants set to zero) is shown in Figure 3 for k_{i1} equal to 8.3×10^{-2}, 2.8×10^{-1}, and 0.83 L/(mol s). Also shown in this figure is the percentage of the catalyst feed that has become deactivated by spontaneous catalyst decay.

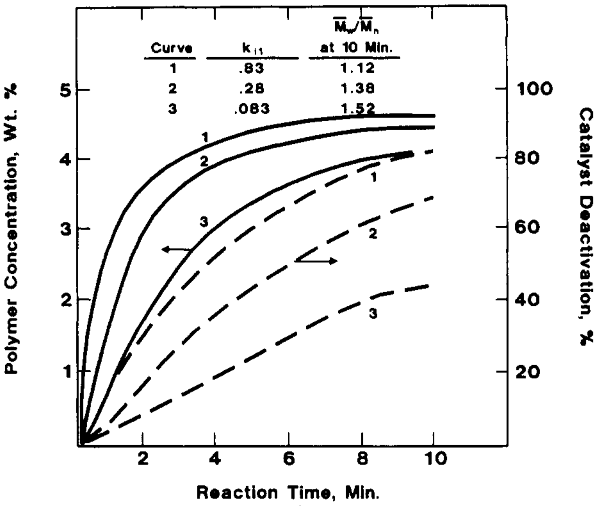


Figure 3. Effect of initiation rate on polymer concentration with no transfer reactions, k_{i1} in L/ms.

About the same polymer concentration is obtained by 10-min reaction time for all three k_{i1} values. However, the polymerization rates are quite different. At a k_{i1} of 0.83 L/(mol s), the slope of the concentration/time curve is at a maximum at or very near to zero reaction time, indicating very fast chain initiation. Despite almost complete deactivation of the catalyst by the end of the polymerization, M_w/M_n is calculated to be 1.12, close to the value for a living polymerization. The reason for this is that most of the chain length is grown at relatively short times as the more reactive ethylene is consumed. Although growth does occur over the full 10 min, >75% of the chain has grown before 30% of the catalyst has deactivated. The other two concentration/time curves in the figure, at the lower values of k_{i1}, show a delay period before reaching the maximum slope, indicative of a reduced rate of chain initiation. But even with slowed initiation ($k_{i1} = 8.3 \times 10^{-2}$) M_w/M_n is only 1.52 which is considerably less than the value of 2.0 that would result in a stirred tank reactor.

Note in Figure 3 that the percent of catalyst feed deactivated by termination reactions drops as k_{i1} is lowered. This is due to incomplete initiation at low k_{i1} values.

For the range of k_{i1} values investigated, M_w/M_n is relatively constant along the length of the reactor (see Figure 4). As shown in Figure 4, 100% catalyst initiation in the 10-min residence time is only obtained at k_{i1} equal to 0.83 L/(mol s). For the other two k_{i1} values, consumption of ethylene by chain propagation causes a continual decrease in initiation rate along the length of the reactor and limits the amount of catalyst that eventually starts chains (chains are postulated to initiate only with ethylene). We also observed that at a k_{i1} of 8.3×10^{-2} L/(mol s) a pseudo steady state in growing chain concentration exists for a considerable period of time during which the rates of chain initiation and termination are about equal. On the other hand, at a k_{i1} of 0.83 L/(mol s), the active chain concentration reaches a maximum very quickly and then decreases for almost the entire polymerization.

The variation in monomer conversion and polymer composition along the reactor is shown in Figure 5 for k_{i1} equal to 0.83 L/(mol s). In view of the much higher re-

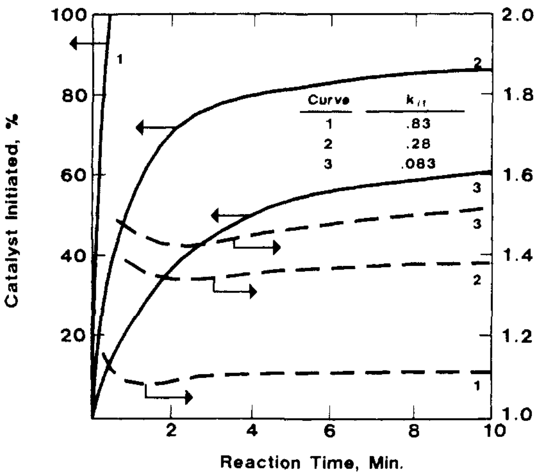


Figure 4. Effect of initiation rate on amount of catalyst initiated and on resultant MWD with no transfer reactions, k_{il} in L/ms.

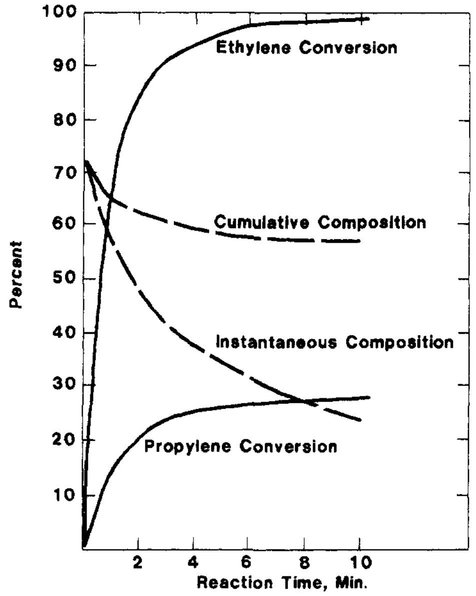


Figure 5. Monomer conversion and polymer composition along the reactor.

Table III
Effect of Spontaneous Chain Termination on Kinetics[a]

spontaneous terminatn const k_t, L/(mol s)	convn, % ethylene	propylene	catalyst	$10^{-3}M_w$	M_w/M_n
8.3×10^{-4}	99.4	30.6	47.6	167	1.05
2.7×10^{-3}	98.4	28.2	83.4	160	1.12
6.9×10^{-3}	91.1	22.9	98.6	141	1.27
9.7×10^{-3}	85.0	20.0	99.7	128	1.36
12.5×10^{-3}	79.0	17.6	100	117	1.43
15.3×10^{-3}	73.6	15.7	100	107	1.49

[a] Results of 10-min residence time.

Table IV
Effect of Hydrogen Chain Transfer on M_n and MWD[a]

H_2 feed, mol/mol of cat.	$10^{-3}M_n$[b]	M_w/M_n
0	161	1.12
0.32	122	1.31
0.48	109	1.39
0.96	82.6	1.58
1.93	55.7	1.82
3.85	33.8	2.04

[a] k_{il} = 0.83 L/(mol h). $k_{trh} = 5.5 \times 10$ L/(mol s). $k_{trm,tra}$ = 0. [b] 10-min reaction time.

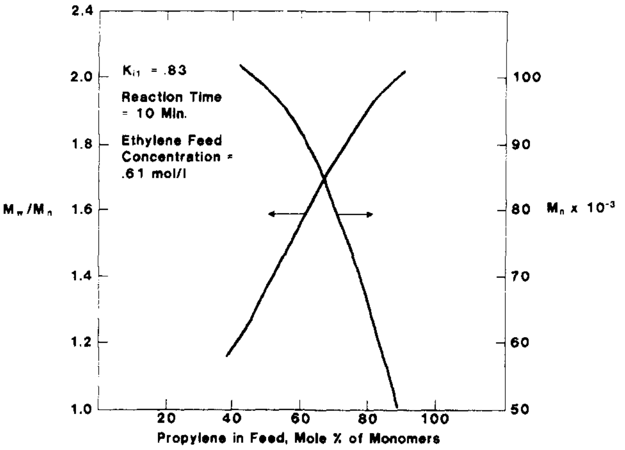


Figure 6. Effect of propylene chain transfer reaction on MW and MWD, rate constants as in Table II, except k_{il} = 0.83 L/ms.

activity of ethylene as compared to propylene, the ethylene/propylene ratio continually drops as the polymerization proceeds, and the copolymer composition becomes enriched with propylene. Although the cumulative polymer ethylene content only varies from 73 to 57 wt % for the example in Figure 5, the instantaneous composition changes much more markedly and the copolymer segments made at 10-min residence time contain only 24 wt % ethylene. Curves of similar shape are generated at a k_{il} of 8.3×10^{-2} L/(mol s). At high k_{il}, however, the CD will be essentially intramolecular in view of the narrow MWD, while at low k_{il} both inter- and intramolecular dispersity will exist to a significant extent.

Increasing the rate of spontaneous chain termination lowers monomer conversion and broadens the MWD, as would be expected. However, the amount of broadening (see Table III) is rather modest for up to a 4-fold increase from the k_t value shown in Table II. At high levels of k_t, significant chain termination is occurring at only moderate ethylene conversion levels, and M_w/M_n increases appreciably, trending toward a value of 2.0 for very large k_t. With initiation fast compared to termination, it appears that this is the maximum breadth observed.

Chain transfer in a plug flow reactor also broadens MWD, as well as lowers polymer molecular weight, and increases the breadth of the intermolecular CD. In the presence of propylene chain transfer ($k_{trm} = 4.2 \times 10^{-3}$ L/(mol s)) raising the mole percent of propylene in the monomer feed from 40 to 90% (see Figure 6) causes M_w/M_n to increase from 1.18 to 2.02 while M_n drops from 120 000 to 50 000.

Thus with a catalyst characterized by this particular set of rate constants it would not be possible to make a very narrow MWD polymer with low ethylene content. M_w/M_n is similarly raised in the presence of hydrogen chain transfer ($k_{trh} = 5.5 \times 10$ L/(mol s)) as illustrated in Table IV. For the k_{trh} value used in the calculations, hydrogen is almost completely consumed by reaction so M_n is inversely proportional to the hydrogen/catalyst ratio.

In cases where the monomer ratio, and thus propagation rate, varies significantly over the course of the reaction, transfer reactions can lead to broadening beyond M_w/M_n = 2. This is not true in radical homopolymerizations, where monomer transfer controls, and polymerization rate and transfer rate are both proportional to monomer concentration. It is the unequal monomer reactivity which leads to broadening here.

The variation of M_n and M_w/M_n with polymerization time is shown in Figures 7 and 8 for propylene and hydrogen transfer, respectively. M_n rises rapidly at first due

Table V
Synthesis Conditions and Characterization Results

sample	cat.	main feed A/V[a]	main feed $C_2^=/C_3^=$ feed ratio, mol/L	$C_2^=$ feed concn, mol/L	sidestream feed $C_2^=$ feed concn, mol/L	inlet temp, °C	exit temp, °C	chains/V, mol/mol	ethylene content	product Lalls M_w, K	Lalls M_z/M_w	elution time M_w/M_n
(14A) 1	VCl_4	15	0.14	0.16	0	−20	−5	0.65	36	217	1.25	1.54
(121A) 2[b]	VCl_4	15	0.19	0.16	0	−20	−7	0.97	44	212	1.98	2.70
(58D) 3	VCl_4	12	0.30	0.24	0	−10	9	0.68	43	129	1.50	1.60
(44A) 4	VCl_4	8	0.17	0.14	0	0	22	0.47	40	143	1.30	1.48
(52A) 5	VCl_4	8	0.17	0.14	0	20		0.48	41	135	1.23	1.57
B 6	VCl_4	8	0.17	0.14	0.039[c]	20		0.46	46	158	1.19	1.58
C 7	VCl_4	8	0.17	0.14	0.039[d]	20		0.44	44	175	1.19	1.61
D 8	VCl_4	8	0.17	0.14	0.039[e]	20		0.49	42	169	1.24	1.69
E 9	VCl_4	8	0.17	0.14	0.039[f]	20		0.49	42	143	1.27	1.65
(75C) 10	VCl_4	12	0.165	0.86	0	−10	0	0.38	39	150	1.23	1.32
(20A) 11	VCl_4	12	0.165	0.86	0	−10	1.5	0.51	41	92	1.20	1.20
(48C) 12	$VOCl_3$	8	0.14	0.16	0	0	3	0.30	38	135	1.40	1.51
(22A) 13	$V(acac)_3$	8	0.11	0.15	0	3		0.10	45	147	1.12	1.26

[a] Al = $Al_2Et_3Cl_3$. [b] In situ catalyst formation, all other premixed. [c] Added at 0.5-s reaction time. [d] Added at 5.9-s reaction time. [e] Added at 10.3-s reaction time. [f] Added at 20.0-s reaction time.

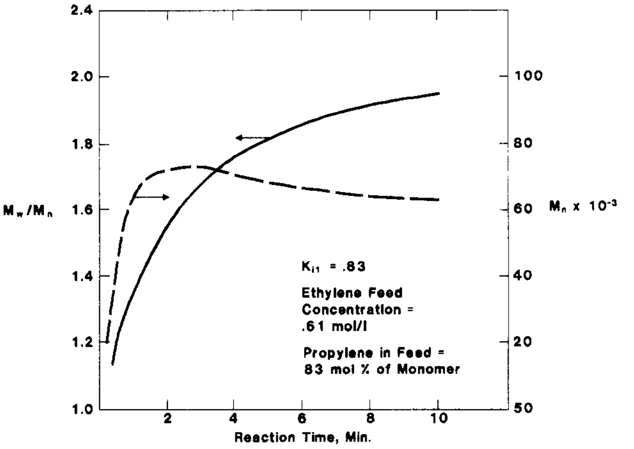


Figure 7. Effect of reaction time on MW and MWD with propylene transfer.

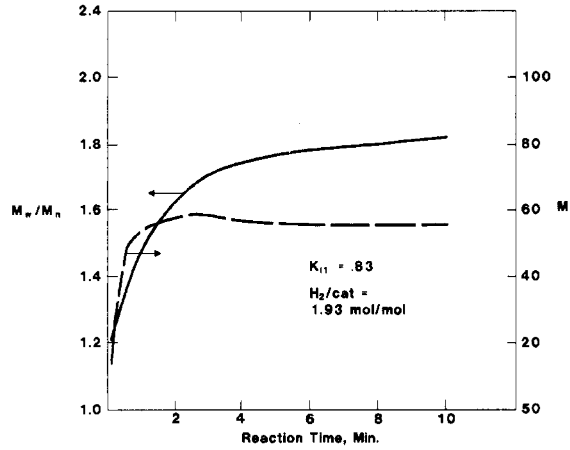


Figure 8. Effect of reaction time on MW and MWD with H_2 transfer.

to the very high propagation rate. However, once most of the ethylene has reacted, the ratio of transfer rate to propagation rate rises, and low molecular weight polymer is produced causing M_n to drop. M_w/M_n increases continually along the reactor length.

These modeling results indicate that EPM copolymerization in a plug flow reactor, operated with a catalyst that produces a single active species and with all the feeds introduced at the start of the polymerization, can produce a polymer with a MWD narrower than that obtained in a CFSTR. To obtain the narrowest possible MWD, initiation of the catalyst must be more rapid than propagation, chain transfer must be minimized, and chain propagation must be much more rapid than chain termination. Furthermore, these narrow MWD copolymers will have a narrow intermolecular compositional distribution and a broad intramolecular distribution. By feeding additional amounts of monomer at various points in the chains' growth, it is possible to vary the monomer compositional distribution along a chain.[12] In comparison, stirred tank EPM's have M_w/M_n limited to a minimum of 2.0 and a narrow intramolecular CD. Thus a plug flow reactor offers an opportunity to make significantly different copolymer structures, if the kinetic requirements for such polymers can be achieved experimentally.

Results

A prerequisite for obtaining narrow MWD polymer is a catalyst system that produces primarily one active catalyst species. On the basis of past work,[13] it was known that soluble catalyst systems prepared from a soluble vanadium compound and $Al_2Et_3Cl_3$ cocatalyst are most likely to meet this requirement. Consequently, our studies focused on catalysts of this type.

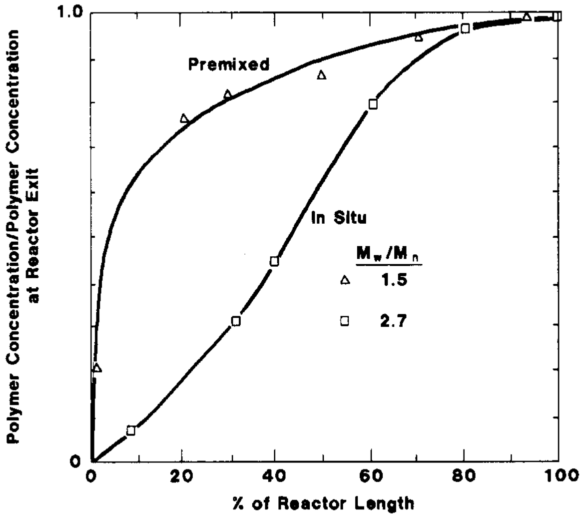


Figure 9. Effect of catalyst component premixing on initiation rate.

Another essential step in the preparation of near monodisperse polymers is fast initiation compared to growth. Initiation rates can be examined by studying polymer concentration versus reaction time using samples taken at various locations along the reactor. Figure 9 shows such results obtained at 20 °C with the catalyst components premixed prior to addition to the monomers as well as mixed at the reactor entrance in the presence of the monomer (in situ catalysts) for the $VCl_4/Al_2Et_3Cl_3$ catalyst system. Typical data are presented in Table V, runs 1 and 2. The increase in polymer concentration along the reactor using premixed catalyst has maximum slope very near zero reaction time, indicating fast chain initiation. The in situ case, on the other hand, shows a delay period before reaching the maximum slope or monomer consumption rate. Comparing these results with those in the kinetic modeling section and with the MWD data of Table V, it is clear that the rate curve obtained in the premixed catalyst is essential to obtain narrow MWD. This is consistent with the simulation data in Figure 3. Similar results can be obtained for $VOCl_3$ and $V(acac)_3$ in combination with $Et_2Al_2Cl_3$ (Table V). All results reported below are for the $VCl_4/Al_2Et_3Cl_3$ system, except otherwise mentioned. Thus, at the proper catalyst premixing conditions isolating the alkylation and reduction (or other alkyl–transition metal) catalyst formation reactions from the monomers can produce soluble V/Al Ziegler catalyst systems that approximate instantaneous initiation and, in addition, contain only a single active species. In fact, when the premixing conditions are optimized, k_{ii} in the reaction scheme of Table I is adequately large so that it appears to have no effect on the observed MWD. The polydispersity of the polymers produced appears to be more due to transfer and termination reactions than slow initiation. This is inferred from studies of MWD breadth versus polymerization temperature and reaction time. MWD broadens rather than narrows as reaction time increases, although even at the shortest times investigated the narrowest MWD is not monodisperse. Also, the fastest reaction rates are always observed near the reactor inlet even as feed temperature is lowered from +30 to −20 °C. If initiation were a factor, its influence should be seen to change over such a significant temperature range.

It is that noted with the premixed catalysts we have tested (in Table V) both propagation and termination rates are faster than with the in situ catalysts studied (Table II). Consequently, polymerization time in these $VCl_4/Et_3Al_2Cl_3$ experiments is much shorter than in the computer simulations discussed above. This has little impact on the modeling results since the ratios of rate constants and not their absolute values control polymer characteristics. The absolute propagation rates vary in the order $VOCl_3 > VCl_4 > V(acac)_3$, all with $Al_2Et_3Cl_3$.

In comparison to the previous work[4-7] on narrow MWD Ziegler-catalyzed polymers, these results show that by premixing the catalyst components, selecting the nature of the components so that only a single active species is generated, and rapidly mixing the preactivated catalyst with the monomers, copolymers with narrow MWD and intermolecular CD can be produced at temperatures much above the prior limit of −40 °C, and there is no need for the absence of ethylene at chain initiation.

Since ethylene is more reactive than propylene, the ethylene/propylene ratio in the reaction mixture continually drops as the polymerization proceeds. As a result, the cumulative polymer ethylene content decreases due to the compositional distribution generated in the polymer. Figure 10 shows the variation in ethylene conversion and polymer composition along the reactor. Since the chains grow uniformly, this compositional distribution is primarily *intramolecular*. Characterization of this distribution is discussed below.

In our experiments, reactor temperature was altered by changing the hexane feed temperature. Raising this temperature from 0 to 20 °C (runs 4 and 5—Table V) gives a higher initial polymerization rate (see Figure 11) but reduces the total amount of polymer produced because of an increased rate of catalyst deactivation. The polymer made at higher temperature also has a lower MW and broader MWD as a result of more termination and transfer.

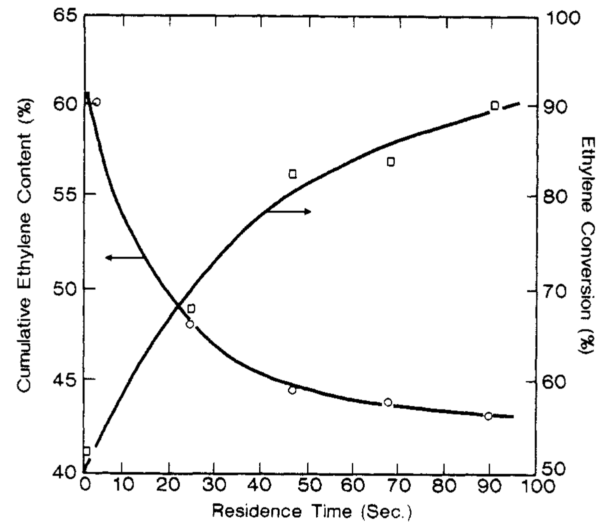


Figure 10. Cumulative polymer ethylene content and ethylene conversion as a function of reaction time. (Samples taken along reactor length.)

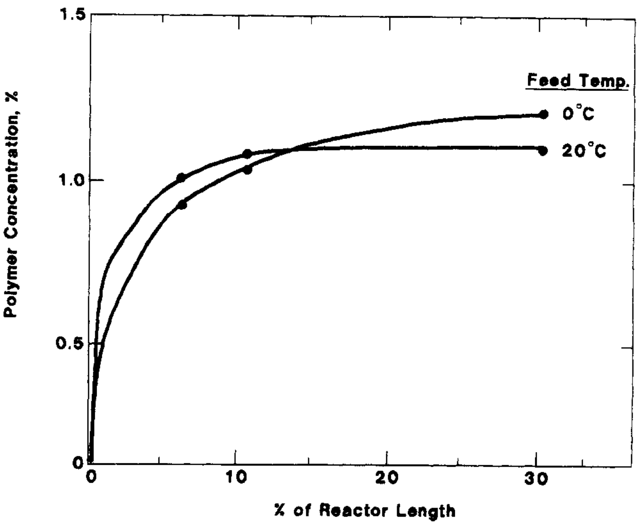


Figure 11. Effect of feed temperature on polymerization rate.

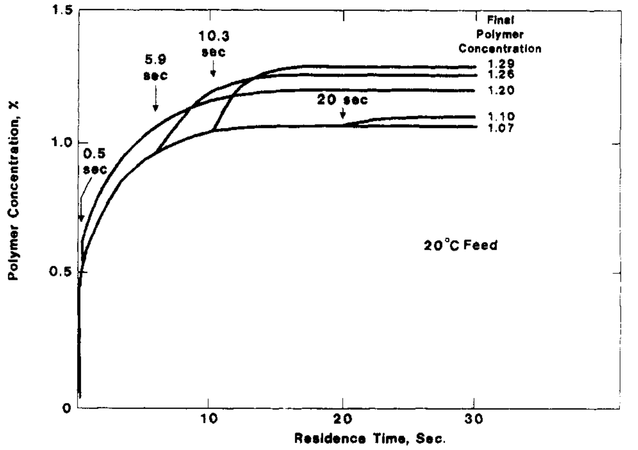


Figure 12. Effect of secondary feeds on polymer concentration. Residence time at second feed point indicated.

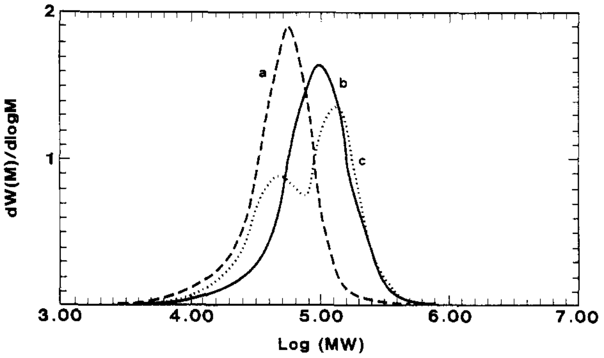


Figure 13. MWD as affected by sidestream feeds: curve a, no sidestream; curve b, sidestream before significant termination; curve c, sidestream after significant termination.

Chain termination rates can be studied by adding additional monomer sidestreams at injection points along the reactor. As shown in Figure 12, (runs 5–9, Table V) at 20 °C feed temperature, a rise in polymer concentration occurs when an ethylene/hexane sidestream is injected at 0.5, 5.9, and 10.3 s residence time. This result in conjunction with both molecular weight increase, no MWD broadening, and ethylene content increase in the final product leads to the conclusion that the majority of polymer chains were still alive at around 11 s. When the sidestream was added at 20-s reaction time, little increase in polymer concentration relative to the base case (no sidestream) was observed. Thus, for this particular set of run conditions the catalyst lifetime is 10–20 s. As can be seen from the final polymer concentrations listed in Figure 12, an optimum in monomer conversion occurs due to the tendency of ethylene to homopolymerize if it is all added near the reactor inlet. The catalyst lifetime has been found to depend quite strongly on the nature of the catalyst components, premixing conditions, monomer feed concentrations, and reactor temperature. When additional monomer is added after a significant portion of the chains have terminated, the remaining chains grow to higher MW than those terminated and multimodal MWD's are produced. This is shown in Figure 13. Hence curve a represents a sample made with a single main feed. Sample b has an additional 166% ethylene added downstream before significant termination has occurred. Sample c has the extra ethylene added after some termination has occurred. The low molecular weight mode in sample c is not identical with the whole polymer of sample a because sample a grew for a longer time than the elapsed time to the secondary feed of sample c. Some termination has occurred in sample a by the time that the peak molecular weight reaches that of the low MW mode of sample c. However without a secondary feed to dramatize this terminated polymer, it only appears as a smooth broadening on the low molecular weight side of the MWD. Termination alone will not produce a multimodal MWD. Below about 40 °C, catalyst lifetime is generally adequate to convert most of the ethylene initially present. As the ethylene is converted, chain growth slows due to the difference in propagation rates between ethylene and propylene. Thus even though the catalyst spontaneously deactivates, the dimunition of average propagation rate that occurs simultaneously prevents appreciable MWD broadening. These experimental results confirm the model calculations, indicating that termination need only be slow compared to propagation to obtain narrow MWD. Figure 12 further indicates that the monomer compositional distribution along a chain can be varied by feeding additional amounts of monomer during the polymerization to influence the polymer composition.

Characterization–Implications for Kinetics. The polymerization results presented above are illustrative of hundreds of experiments run in our laboratories since 1980. Routine characterization included measurement of Mooney viscosity, average ethylene content, and molecular weight by size exclusion chromatography with on-line light scattering. Some polymers of special interest were also examined by differential scanning calorimetry, ^{13}C and ^{1}H NMR, solvent–nonsolvent fractionation, mechanical spectrometry, capillary rheometry, and creep measurements.

A qualitative summary of these results is given, and then detailed examples are presented on selected samples.

Polymers have been prepared, with narrow MWD, with weight-average molecular weights ranging from about 10^4 to above 10^6. The lower bound of MW where MWD must begin to broaden due to a presumed overlap of initiation with growth, finite chain size statistics, or convective mixing effects has not been detected.

The molecular weight range over which the polymers are prepared is controlled by the monomer to catalyst ratio, by the time at which the reaction is quenched, and in some cases by catalyst deactivation at elevated temperature. Depending somewhat on premixing conditions, the fraction of the vanadium that is active for chain growth is ca. 0.1 for $V(acac)_3/Et_3Al_2Cl_3$ and 0.4 for $VCl_4/Et_3Al_2Cl_3$. The former result is similar to that obtained by Doi et al.[4] Doi's early unsuccessful work[11] with VCl_4 and $VOCl_3$ did not provide comparable results, neither did Junghanns et al.[10] The exact fraction of the vanadium that is active appears to be influenced by the presence of ethylene at initiation, and the catalyst effectiveness increases with ethylene concentration.

Polymers with average weight percent ethylene composition ranging from 0 to 75% have been prepared by varying the feed composition. The polypropylene prepared with $VCl_4/Et_3Al_2Cl_3$ does not have a narrow MWD. Two modes appear, one low in molecular weight and atatic and another at least 2 orders of magnitude higher, which presumably is isotactic[11] since it precipitates from hexane solvent causing the reactor to foul. When ethylene is present this bimodality does not appear. The upper bound on average ethylene composition that can conveniently be made is set by polymer solubility as controlled by the amount of crystalline ethylene sequences. Severe reactor fouling generally occurs at weight feed ratios of propylene to ethylene less than 0.5:1.0. In principle, there appears to be no reason why narrow MWD polyethylene cannot be made if reactor fouling is prevented. In view of the very high ethylene homopolymerization rate, however, rapid mixing and initiation become more critical to obtain narrow MWD.

When the polymers are made with a single feed and are permitted to react to a significant monomer conversion, a compositional heterogeneity exists, which will be shown below to be predominantly intramolecular. The primary manifestations of this heterogeneity in routine testing are increased crystallinity and melting temperature at a given average ethylene as compared to a backmixed reactor product. This is completely expected[13] on the basis of previous studies of heterogeneity. Similarly, ^{13}C NMR parameters such as N, the average length of sequences greater than or equal to three ethylenes,[30–32] is larger than that anticipated for a homogeneous product for the average composition and reactivity ratios.

There are no easily observable effects of the compositional heterogeneity on viscosity molecular weight rela-

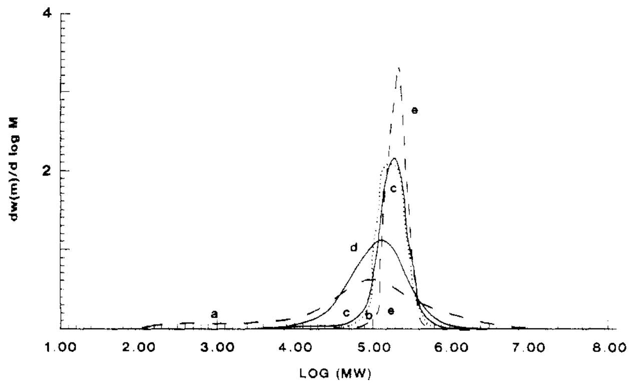


Figure 14. GPC system performance illustrated with several chromatograms. See text for identification of samples a–e.

tionships nor is there pure polymer phase separation other than the aforementioned crystallinity.

If the polymerizations are quenched at low conversion, e.g. <20% ethylene conversion, the monomer ratio has remained essentially constant, temperature rise is only a few degrees during polymerization, and reactivity ratios can be estimated by nonlinear least-squares fits to the standard terminal model copolymerization equation.[3,13] For $VCl_4/Et_3Al_2Cl_3$ at 30 °C r_1 is evaluated to be 8 and r_2 0.02, with ethylene as the one monomer. This result is not far from previously published values,[13,33] indicating that the premixing has not changed the nature of the catalyst in this regard. We have neglected the complications due to propylene inversions here.

Our estimated rate constants, heats of polymerization, and specific heat values have been incorporated into the computer model discussed above, in order to calculate the instantaneous conversion and thus instantaneous composition along the polymer backbone. These model results have been found to agree well with the cumulative compositions measured along the reactor. In cases where multiple sidestream monomer feeds are employed, computer simulation is the only practical means to estimate the overall detailed polymer structure.

The narrowest MWD and intermolecularly most homogeneous samples are prepared under conditions where turbulent mixing is best and the polymerization is intentionally terminated below 30 °C. Both catalyst deactivation and transfer with propylene have substantially higher activation energies than the propagation reactions with the aforementioned catalysts. Consequently, the upper limit for *uniform* growth is in the 40–50 °C range for catalyst components we have studied to date. This polymerization temperature represents an increase of about 80 °C over the previous studies[4] to produce narrow MWD with Ziegler catalysts.

The narrowest MWD samples are narrow enough to test the resolution and dispersion characteristics of chromatographic analysis process. The MWD results presented in Table V, although accurately reflecting trends in the product characteristics, are biased high on an absolute basis. (Three significant figures are reported only to distinguish samples.) Selected samples have been studied in more detail for the influence of chromatographic variables. Results of one such study are presented in Figures 14–19.

As routinely run in our laboratory, the chromatography experiment injects ca. 0.6 mg of polymer onto four 25-cm Shodex columns. At least such an injection amount is needed to distinguish low percentages (e.g. 1%) of the total polymer in the tails of an MWD. Such a result is shown in Figure 14, curve a, for a $VOCl_3/Et_2AlCl$ polymer prepared in a backmixed reactor. This clearly shows the MWD range detection capability. Analysis of narrow MWD polymer at this injection mass, when properly polymerized as discussed above, reveals no polymer in "tails" of the distribution as detected by either the differential refractometer, Figure 14, curves b and c, and or light scattering detector, Figure 15. Also included for reference in Figure 14 are backmixed reactor, single species catalyst[13] samples JBG 11(d) which was previously used in a study of model hydrogenated polyisoprenes,[21] and a commercially available polystyrene standard (e) (TSK Standard F-40 Batch TS-85). At these injected amounts, which provide good signal to noise in the tails of the MWD, there are significant concentration effects on coil size and thus elution volume and presumably other aspects of the separation process.[34] Thus the peak height can be suppressed due to loss in resolution, and parameters such as M_w/M_n and M_z/M_w can be raised. At reduced injected mass such "overloading" is diminished but diffusional broadening remains. There is also the question as to whether loss of signal intensity in the tails of the peak alters the apparent calculated MWD. The fact that the LALLS detector has a proportionately greater sensitivity at high MW than the DRI and vice versa, and that interdetector lags must be corrected for also influences results. For these reasons unknown samples are best studied in comparison with known commercially available standards or previously characterized polymers whose properties have been disclosed in the literature.

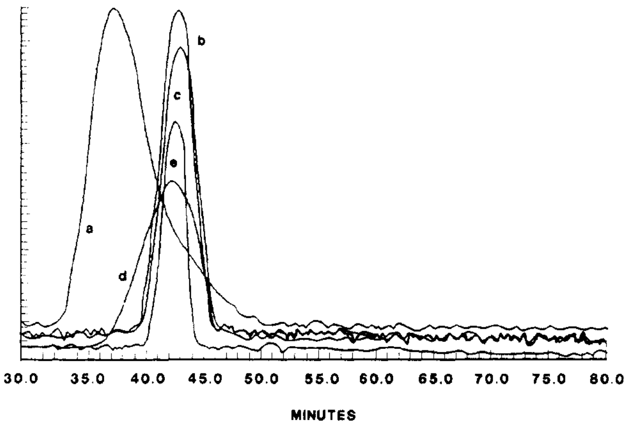
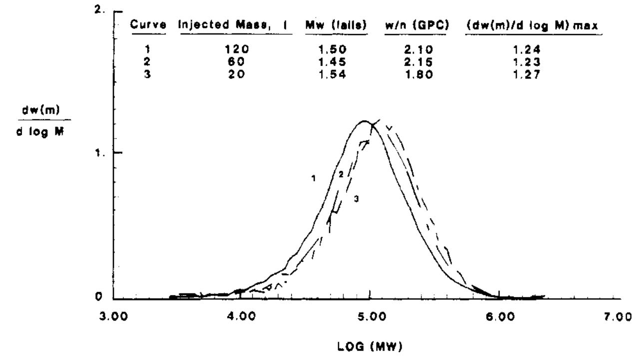


Figure 15. LALLS detector output for the same samples as Figure 14.



Curve	Injected Mass, I	Mw (lalls)	w/n (GPC)	(dw(m)/d log M) max
1	120	1.50	2.10	1.24
2	60	1.45	2.15	1.23
3	20	1.54	1.80	1.27

Figure 16. GPC performance for most probable MWD samples as injected mass is decreased. Peak maximum height and MW by LALLS are invariant.

We varied injected mass over a 12-fold range for JBG 11, F-40, and the plugflow reactor sample b of Figure 14 (designated 87-8). It can be seen from Figure 16, for the backmixed reactor product, that although there is a shift in elution volume at low injected mass, neither $dw(M)/d \log M$ nor M_w/M_n changes substantially. M_w by light

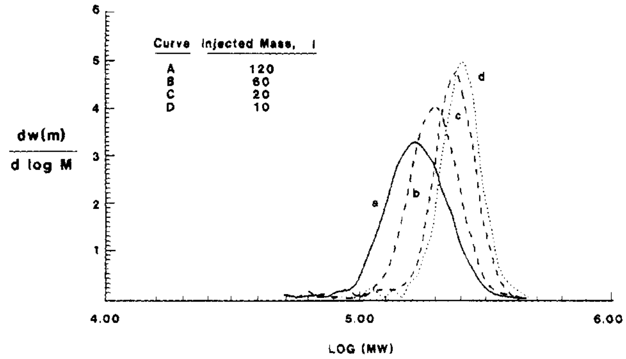


Figure 17. GPC performance for narrow MWD polystyrene standard F40 as mass is decreased.

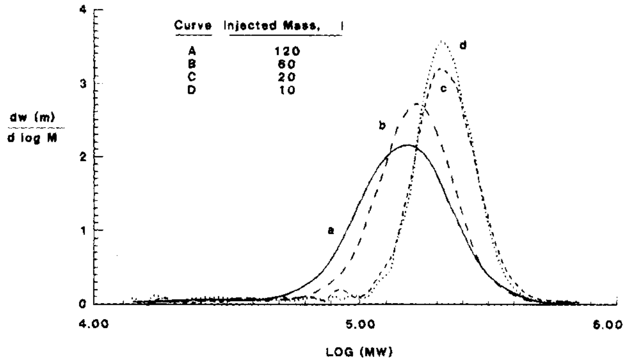


Figure 18. GPC performance for narrow MWD EPM prepared as described in text.

Table VI
Infinite Dilution Chromatographic Results

sample	M_w/M_n	$(dw(M)/d\log M)_{max}$	$(M_z/M_w)^{LALLS}$	anticipated M_w/M_n
JBG 11	2.2	1.25	1.8	2.0 for CSTR
87-8	1.16	4.0	1.1	
F-40	1.05	5.3	1.1	1.02 from specification sheet

scattering $\bar{M}_w$ is invariant at about 1.5 × 10^5 g/mol. As can be seen from Figures 17 and 18, there are substantial changes in the results for the narrower distribution samples. The results can be extrapolated to zero injected mass with the results as shown in Table VI and Figure 19. MW from LALLS remains invariant in these experiments. These elution time results are presented in terms of apparent MW on an EPM basis.

The conclusion of the chromatographic analyses is that operation in the injected mass region used to obtain the results in Table V adds approximately 0.03 units to M_w/M_n. Furthermore even at infinite dilution residual broadening may be adding another 0.03 unit. It probably is significant that M_z/M_w of sample 87-8 is closer to the PS standards' value we obtained than is M_w/M_n. Transfer reactions can produce low MW material, substantially decreasing M_n. Slow initiation and termination, as well as transfer, can effect the shape of the distribution on the high MW side, but with the plug flow reactor residence time distribution there is not a finite probability of very long residence time for some fraction of the chains as in a CSTR. Thus the high MW side of the distribution is more likely to be cutoff sharply than is the low side. This should have significance in rheological response which depends on high MW moments. The MWD of sample 87-8 is very narrow but not as narrow as anionically prepared polystyrene standards.

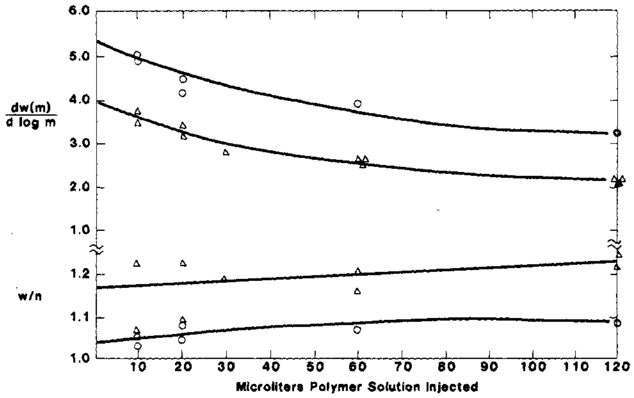


Figure 19. Extrapolation of MWD parameters to zero concentration operation for the GPC.

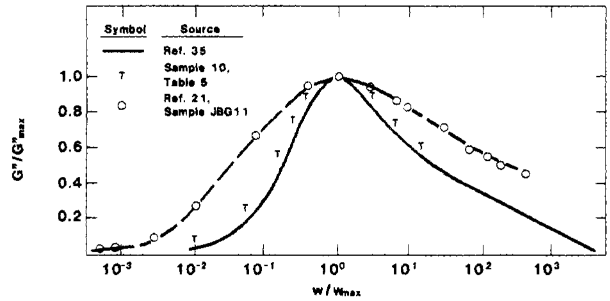


Figure 20. Loss modulus normalized by its maximum in the terminal region as a function of frequency, reduced to the frequency at the maximum.

Table VII

sample	$10^{-5}M_w$	M_z/M_w	M_w/M_n	J_e^0/G_N^0 [b]	G_N^0/G''_{max}
10	0.9	1.1	1.2	3.5	5.1
11	1.5	1.3[a]	1.3	5.0	5.4
JBG 11	1.6	1.7	2.0	>16[c]	
hydrogenated PIP					
HPI-1.115L[d]	1.55	1.05	1.1	2.1	

[a] 75C has slight high MW shoulder in LALLS chromatogram. [b] Data on 10 and 11 taken as G_N^0 from plateau on same data set from which J_e was obtained as $G'/(G'')^2$. [c] Really not measurable. G' not linear yet at 10^{-3} rad/s. The very fact the Je can be measured on the plug flow reactor polymers makes them radically different from CSTR samples. [d] Prepared anionically, $J_e^0G_N^0$ measured by J. Gotro.[21]

The residual breadth is due to some combination of slow initiation, termination, and propylene or alkyl transfer reactions and perhaps in part to mixing in the reactor at initiation and at quench. We do not believe that we have yet reached the absolute limit inherent to the catalysts.

A reasonable question is whether the residual breadth is of any practical consequence. Rheological properties are very sensitive measures of MWD and topological characteristics. Graessley and co-workers[35] have shown that the linear viscoelastic loss modulus as a function of frequency in the terminal region has a characteristic limiting form for narrow MWD flexible polymers. Also, the product of the recoverable compliance, J_e^0, and plateau modulus, G_N^0 reaches a limiting low value. We have performed such measurements and compare the results to those obtained on hydrogenated polyisoprenes, i.e. model EP's.[21]

Results are presented in Table VII and Figures 20 and 21. Figure 20 presents the Graessley[35] reference data, the JBG 11 sample prepared in a backmixed reactor, and data on sample 87-8 and sample 10 as described in Table V. Figure 21 presents the superposed frequency sweep data on sample 87-8. By these measures the MWD is obviously again determined to be very narrow. A value of 3.5 for

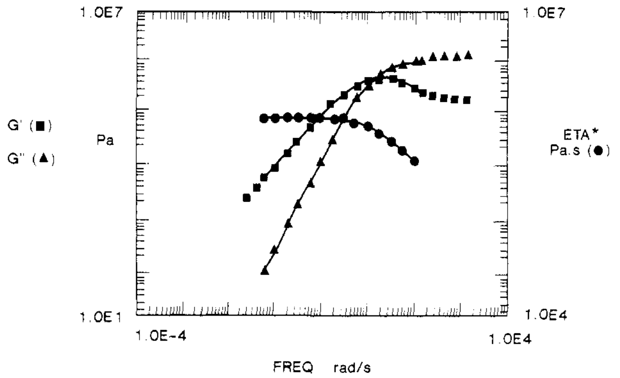


Figure 21. Storage and loss modulii and dynamic viscosity as a function of frequency superposed to 120 °C, sample 87-8.

$J_e{}^0G_N{}^0$ was once thought to be about as low as could be reached,[36] although as preparation techniques improved still lower values were obtained.[21] The plateau modulus obtained by integration over G'' for samples 10 and 11 of Table V is found to be ca. 1.6×10^5 dyns/cm^2, in agreement with previous studies.[3,21] For these same two samples, using the rule $G_N{}^0 = 3.5G''_{max}$,[21] we obtained $G_N{}^0 = 1.1 \times 10^7$, residual breadth is again detectable.

There seems to be little effect of the intramolecular compositional distribution on these mechanical properties. The samples behaved similarly to CSTR or the HPI polymers when kept above their crystallization temperature.

Comparison of the undiluted polymer viscosity at a given molecular weight with results given in ref 3 and 21 indicates these polymers to be close to the results for hydrogenated polyisoprenes and somewhat below conventional backmixed EP copolymers. Furthermore the results of gravity driven creep experiments[23] yield viscosities systematically larger than from the mechanical spectrometer. The latter bias is approximately 25% and is not yet resolved. The bias with backmixed reactor samples is at least a factor of 2 and may be due to long chain branching in the CSTR copolymers. A possible mechanism for this has been discussed.[7] It may involve unsaturated end group copolymerization.

We conclude from these MWD studies that in processing operations the product should behave very similarly to anionically prepared polybutadienes of narrow MWD. The plateau modulus is similarly high, and the relaxation spectrum is similarly narrow. Whether further narrowing would produce practical changes in rheological response remains to be determined.

Finally, we address the question of intramolecular heterogeneity. As in the case of the MWD studies, we have examined a variety of samples but report detailed results on only one. Polymer prepared with a single monomer feed and polymerized to high conversion is anticipated to have a broad intramolecular compositional distribution. For example, starting a polymerization at ca 10:1 propylene to ethylene monomer weight ratio will begin the chain with an instantaneous composition in the 60 wt % ethylene range. Toward the end of the reactor when most of the more reactive ethylene has been converted and the monomer ratio has changed substantially, the instantaneous polymer composition can drift to below 30 wt % ethylene.

Measurement of the cumulative ethylene content as in Figure 10, coupled with the knowledge that the MWD is narrow, is tantamount to proof that the compositional distribution is intramolecular.

However, we have run the following experiment to generate additional evidence. A sample was subjected to a solvent–nonsolvent fractionation. By adjusting titration conditions fractions of 10–20 wt % of the total polymer were obtained and the average composition was measured. Such results are presented in Figure 22. One "center-cut" fraction was refractionated with no further compositional heterogeneity detected (curve ■). This polymer was then heated, under N_2, to 320 °C for approximately 30 min to degrade the chains. The exact time and temperature must be determined empirically on the basis of the ethylene content of the polymer. Ethylene sequences are more resistant to thermal degradation than propylene sequences. Conditions were chosen to obtain a final product MW of 3000–5000 when the starting polymer was MW > 10^5. The MWD broadens during this process toward a most probable ($M_w/M_n \sim 2$). Refractionation of this product with determination of composition produces curve ▲ in Figure 22. An intermolecular compositonal distribution is now detected where none was observed before. This is due to the fact that the different composition portions of the chain have been separated from one another. Computer simulation of the compositional distribution in this particular sample, 11, indicates the chain should start at about 65% ethylene and end with segments below 20% ethylene, for an average of about 41% at M_w 92 000. The fractionation obviously did not detect this wide a range in this particular case.

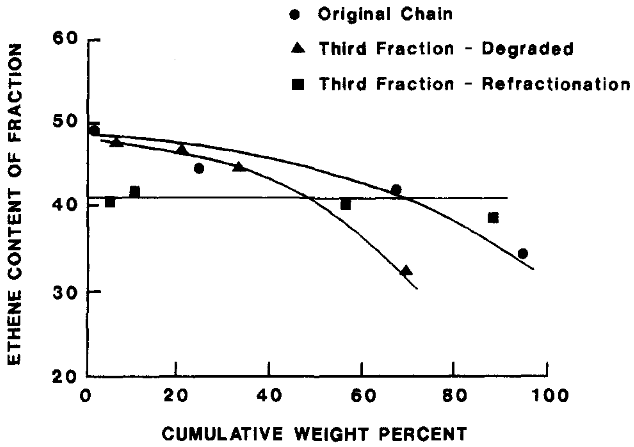


Figure 22. Fractionation data demonstrating intramolecular heterogenity.

Arguments can be made as to whether the total compositional distribution is revealed by such a procedure. One needs to look at chain sections large enough so that the normal statistical distribution of monomer units has been attained, e.g. 100 units, MW 3500. If the monomer ratio is changing so fast that substantial compositional change occurs over a shorter range than that, then the full compositional distribution will not be detected even if the fractionation were perfect, which it is not. It is convenient that in the ethylene–propylene case that both high ethylene and high MW contribute to insolubility in hexane–2-propanol. Since the high ethylene segments tend to degrade less, there is a bias which helps the detection. The major point of Figure 22 is that a fraction which does not undergo further separation upon refractionation does reveal additional compositional heterogeneity after degradation. Much of the detail of the detection of such composition is relevant for legal issues.[12] If structures are prepared by using multiple-feed points along the reactor or multiple feeds at varying times in a batch reactor, analysis of the whole polymer after preparation is not really adequate to fix the structure. Either samples must be taken during the polymerization or a combination of monomer conversion results and reactivity ratios must be used to calculate the contour composition.

If the above experiment is run on a copolymer prepared in a backmixed reactor, with the same catalyst, 95 wt % of the sample is within ±3% of the mean ethylene composition both before and after degradation. The sample's ethylene composition is not changed by the thermal degradation process.

Conclusions

We have presented polymerization and characterization data that demonstrate that narrow molecular weight distribution, intramolecularly heterogeneous ethylene–propylene polymers can be prepared. Unlike previous studies, this can now be done at temperatures up to at least 40 °C. The key to narrow MWD in ethylene and propylene copolymerization with vanadium halide catalysts is premixing of the aluminum alkyl and vanadium components prior to contacting with the monomers so that initiation is isolated from propagation. Furthermore the polymerizations are very rapid at such elevated temperatures and mixing of reactants must be substantially completed in tenths of seconds or less to avoid undesirable heterogeneity.

The ability to prepare narrow MWD and compositionally tailored polymers has considerable commercial significance. For elastomer applications narrow MWD offers the opportunity to produce high number average molecular weight polymer, for low chain end defect crosslinked networks, at a given bulk viscosity for the precross-linked polymer. Narrow MWD polymers have increased mechanical stability in lubricating oils when compared to broader polymers of the same effectiveness in their ability to raise the formulated oil viscosity. Such ethylene–propylene polymers can effectively compete with anionically prepared and hydrogenated poly(styrene-*co*-isoprene) block polymer on this basis. Finally, appropriately designed intramolecular compositional distributions can lead to useful activity in polyolefin blends and in polymer solution properties.

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Registry No. E, 74-85-1; P, 115-07-1; (E)(P) (copolymer), 9010-79-1; VCl_4, 7632-51-1; $VOCl_3$, 7727-18-6; $V(acac)_3$, 13476-99-8; $Al_2Et_3Cl_3$, 12075-68-2.

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