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Block Copolymers of Polyethylene and Ethylene−Propylene−Diene Elastomer. Synthesis, Characterization, and Properties

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ABSTRACT: PE−EP and PE−EP−EPDM block polymers have been made in yields exceeding 70% with Ziegler−Natta catalysts by matching the polymerization time for each block to chain growth time and catalyst decay rates. A short residence time tubular flow reactor with multiple side stream feeds was used to accomplish this result. The amount of block polymer and chain fragments in the product was quantified by various techniques including DSC, solvent fractionation, and GPC/FTIR. PE−EP diblocks have low strength, as expected, and are not suitable for most TPE applications. However, PE−EP−EPDM triblocks with optimized EPDM block length could be coupled via olefinic unsaturation in the EPDM to form multiarm starlike structures consisting of a central elastomeric core with the PE blocks extending outward. The coupled triblocks gave processible polymers with tensile strengths of 12−18 MPa and tension sets less than 10%.

Introduction

Since the early discovery that some Ziegler−Natta (Z−N) catalyst systems retain almost undiminished activity over extended periods of time, a considerable effort has been expended trying to make α-olefin block copolymers of various types. Certainly, materials of this nature could have very desirable properties, especially if A−B−A triblocks could be synthesized with crystalline end blocks and an elastomeric midblock to provide low cost thermoplastic elastomers (TPE). Attempts at Z−N-catalyzed block polymerization used essentially the same method developed for living anionic block copolymers: the catalyst is exposed to a first monomer for a period of time, then a second monomer, and so on until the desired block structure is obtained. A good description of this approach is given by Bier et al.[1] However, β-hydride and monomer chain transfer are characteristics of most Z−N catalysts, and chain lifetimes are quite short. As a result, unless great care is taken to match the monomer addition cycle with the chain lifetime, the sequential monomer addition technique primarily produces a mixture of homopolymers with relatively little block polymer present. Boor[2] reviewed most of the early attempts to produce block polymers and concluded it was unlikely that appreciable amounts were formed. Kresge[3] has more recently summarized the difficulties inherent in producing polyolefin block copolymers with Z−N catalysts.

Busico et al.[4] tried to make a diblock polymer of (polyethylene-*b*-ethylene propylene) copolymer (PE−EP) with a $TiCl_3$ (AA)/$AlEt_2Cl$ catalyst system in gas-phase polymerization with a monomer feeding cycle of 10−20 s. At 1 atm of monomer pressure in the reactor, analysis of the polymer indicated that a homopolymer mixture was the major product. Thus chain lifetimes were indicated to be significantly less than 10−20 s. However, in a second study in which monomer pressure was reduced to 0.10 atm, Busico et al.[5] found that chain lifetime increased considerably, and the desired diblock polymer was obtained as confirmed by extraction studies. Catalyst activity at these conditions was very low.

$V(acac)_3$−aluminum alkyl catalyst systems have living character at very low temperatures (<−65 °C), and Evens and Pijpers[6] were able to produce a triblock with syndiotactic polypropylene (sPP) end blocks and an EP copolymer midblock. However, the triblock was contaminated with polypropylene homopolymer and the PP block was not crystalline enough to give a TPE. Due to chain transfer, it was not possible to make a PE−EP−PE triblock. Doi and Ueki[7] carried out a similar polymerization, but by addition of anisole to modify the catalyst, they were able to eliminate the homopolymer and make a pure sPP−EP−sPP triblock with an M_w/M_n of 1.24. Because of the low polymerization temperature needed to get a living polymer with $V(acac)_3$ and

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the low catalyst activity, polymerization under these conditions is not commercially attractive.

Lock[8] discovered that propylene polymerization catalyzed by $TiCl_3$ activated with certain titanocene compounds had living characteristics. The catalyst activity remains unchanged after more than 17 h, and the polymer molecular weight is linearly related to polymer yield. Lock used a sequential monomer addition method to produce triblock polymers with isotactic polypropylene end blocks and an ethylene−propylene copolymer mid-block iPP−EP−iPP. Analysis of the polymer by solvent fractionation indicated that 66% of the EP was chemically bonded to iPP, but it was not possible to determine the relative amounts of diblock and triblock polymer. Also, the MWD of the polymer was broad, with M_w/M_n between 4 and 5, and the EP block was very compositionally heterogeneous. At an average ethylene content of about 55 wt %, DSC analysis indicated the presence of both polyethylene and semicrystalline EP copolymer. These characteristics were attributed to the presence of multiple active catalyst species. The block copolymers had reasonably good TPE mechanical properties at room temperature, but at 70 °C the properties were appreciably reduced despite a 150−160 °C melting point for the iPP block. This might indicate that the polymer had a large fraction of diblock polymer with a semicrystalline EP section which melted below 70 °C, rather than the desired triblock.

Mori et al.[9] prepared an iPP−EP diblock polymer in a tubular flow reactor with short residence time (0.065−0.130 s). Propylene dissolved in toluene and a supported titanium catalyst were fed to the reactor inlet to form the iPP block, and an ethylene solution in toluene was added partway down the reactor to form the EP. Absence of a soluble fraction after extraction of the polymer at room temperature with heptane was cited as evidence for high block polymer yield. However, since the EP composition was not determined, lack of a soluble fraction could equally well be due to the formation of semicrystalline EP copolymer, insoluble in heptane, as indicated by Lock's[8] results.

The synthetic requirements for producing a polymer that has a broad intramolecular composition distribution (CD) along the chain contour and a narrow intermolecular CD are well recognized. Desirably, only one type of active site is present, all of the chains initiate growth at the same instant, chain transfer is absent, and the active site is living. Living polymers made under these conditions in a batch or plug flow reactor will also have a very narrow MWD with M_w/M_n close to 1.0. Work by Ver Strate et al.[10] demonstrated that ethylene propylene copolymers with characteristics approaching that of living polymers could be produced with certain soluble vanadium based Z−N catalysts that are not living, as long as the polymerization rate is significantly higher than the site termination rate. We denote polymerization under these conditions as "pseudo living". EP with M_w/M_n as low as 1.2 and a narrow interchain CD was obtained by solution polymerization in a tubular reactor under these conditions. (Narrow MWD EP made by this process is commercially available from the Exxon Chemical Co. as Vistalon 878 and 919.) By addition of feeds of different comonomer composition along the reactor length, chain structures were obtained with varying degrees of intrachain CD.

We have now examined whether the same technique can be used to produce poly(ethylene-*b*-ethylene propylene) (PE−EP) block copolymers in high yield. Essentially the same catalyst and tubular reactor system were used as described in the previous work by Ver Strate et al.;[10] however, to make the block polymer, only ethylene was fed to the reactor inlet, and then part way down the reactor, after the PE block had grown to the desired length, additional feeds of mixed ethylene and propylene were added to produce the EP block. This polymerization differs significantly from the previous solution polymerization in that the PE block precipitates from solution initially and then is partially solubilized by the addition of the EP block. Diblocks of this kind have potential application as impact modifiers for plastics, tougheners in bitumen, and components in hot melt adhesives. However, for thermoplastic elastomer applications, PE−EP−PE triblocks are most desired.

Such triblocks cannot be easily made by the process described here. Soluble vanadium catalysts do not polymerize propylene well, and once propylene is introduced into the reactor, unreacted propylene cannot readily be removed for growing the final PE end block. To get around this problem, triblocks were produced of PE, EP, and then an ethylene, propylene, and ethylidene norbornene terpolymer (EPDM) end block by introducing the diene into the reactor close to the reactor exit. The EPDM block has a number of reactive olefinic sites. When the EPDM blocks are coupled postreactor, a nodular polymer is produced which contains a central elastomeric EPDM nodule with EP−PE arms extending radially outward. Some of the properties of PE−EP−EPDM block polymers were described in an earlier publication by Cozewith et al.[11] In this report we focus on the synthesis and characterization of the polymers. It was possible to produce a high yield of block polymer as compared to homopolymer chain fragments, and the product can be produced in a continuous flow tubular reactor. Evaluation of the properties of these polymers indicated attractive TPE characteristics.

Experimental Section

1. Synthesis. A. Materials. Hexane. Polymerization grade hexane (approximately 85% *n*-hexane) from Phillips Petroleum Co. was purified over silica gel (PA-400, W. R. Grace) and 4-A molecular sieves (Union Carbide, $^1/_{16}$ in. pellets).

Ethylene. Polymerization grade ethylene from Matheson Co. was purified over 4-A molecular sieves.

Propylene. Polymerization grade propylene from MG Industries was purified over PA-400 silica gel and 4-A molecular sieves.

Ethylidene Norbornene (ENB). ENB from Union Carbide Co. was purified over 4-A molecular sieves.

Catalysts. VCl_4 (Stratcor) and $Al_2Cl_3Et_3$ (Albermarle) were used as received.

B. Polymerization. The polymerization equipment and procedure was essentially identical to that described earlier by Ver Strate et al.[10] Catalyst (VCl_4) and cocatalyst ($Al_2Cl_3Et_3$) were prepared as separate solutions in hexane and maintained in vessels pressurized with nitrogen. These solutions were metered in the desired ratio through flow control valves and combined in a mixing tee along with additional hexane to give the proper flow velocities for optimum mixing. The combined feeds then passed through a coil immersed in a thermostated bath to allow active site initiation at the desired residence time and temperature. Typical initiation conditions were 12 s at 10 °C with Al/V ratios of 6−8 mol/mol.

Ethylene, propylene, and hexane feeds were piped to the reactor under pressure from a pilot plant building utility system. ENB dissolved in hexane was fed from a nitrogen-pressurized vessel. Five parallel feed systems consisting of flow control valves, differential pressure flow instruments, and associated feed blending valves were available for the initial reactor feed and up to four side stream feeds. Monomers were added to the hexane upstream of the reactor feed inlets, and the combined stream passed through a coil in a thermostated bath to adjust the feed temperature and provide enough time for monomer dissolution before the feed entered the reactor. A pilot plant computer system controlled feed rates and temperatures as well as logging all operating data. The initial and side stream feeds were delivered to the reactor through mixing tees, and the tee size and hexane flows were adjusted to give optimum mixing according to the criteria established by Cozewith and Busko.[12] The reactor was constructed of 1220 mm lengths of $^3/_8$ in. (9.52 mm) tubing with a nominal ID of $^5/_{16}$ in. (7.94 mm) connected by large radius U-bends. Each length contained two tees for feed introduction, and tee locations were chosen to give the desired residence time at a side stream feed point. The overall reaction time was set by adding a 2-propanol/hexane quench solution to the reactor at one of the side stream tees.

The first reactor section was constructed of glass tubing so that the state of polymer solubility during polymerization could be observed. Typically PE particles slowly collected on the wall near the catalyst inlet. When the accumulation was big enough to affect reactor operation, it was removed by a specially designed plunger. West et al.[13] have discussed the details of the design of the glass tubular reactor. The remaining sections of the reactor were constructed from stainless steel tubing. The reactor was not insulated or jacketed, and reactor temperatures were normally close to ambient (20−28 °C). Reactor pressure was set at 300 KPa to maintain the monomers in solution at the reactor temperature. The reactor effluent passed through a pressure control valve to reduce the pressure to atmospheric and partially flash unreacted monomers which were vented from the top of a monomer separator vessel. The polymer product, as a dispersion in hexane, was removed from the bottom of the vessel, stabilized with antioxidant, and vigorously mixed with dilute aqueous HCl (0.1%) to extract catalyst residues. Following separation of the aqueous phase, the hexane phase was slowly poured into boiling water to flash off hexane and monomers and precipitate the polymer. Mill or vacuum-drying was then used to remove water and produce dry polymer for analysis.

2. Characterization. Ethylene Content. Ethylene content was measured by FTIR by ASTM procedure D3900 in conjunction with the calibration described by Gardner et al.[14] This procedure was revised in 1994 by switching to a calibration based on standards analyzed by ^{13}C NMR. The new calibration gives about 8% (relative) higher values for ethylene content for the same value of the 720 cm^{-1}/1154 cm^{-1} peak ratio.

ENB Content. ENB was measured by FTIR according to ASTM procedure D6047.

Mooney Viscosity. ASTM D1648 was used to determine Mooney viscosity at 150 °C.

Molecular Weight. Molecular weight was measured by GPC (Waters, 150 °C) with a combination of refractive index (DRI) and online low angle laser light scattering (KMX-6 Chromatix-Milton Roy) detectors. Details of the procedure have been given by Ver Strate et al.[10] For the polymers discussed in this work, there was negligible difference in M_w measured by the two different methods.

GPC/FTIR. GPC/FTIR analysis was carried out with the procedure described by Faldi et al.[15] The GPC effluent is split into two parts, one of which is sent to the DRI detector for molecular weight measurement, while the other is sprayed onto a rotating disk kept in an oven. The solvent (1,2,4-trichlorobenzene) evaporates, leaving a track of solid polymer on the disk. The position of polymer in the track is related to the GPC elution time, and composition at each position is determined by FTIR analysis. Polymer analysis was carried out with a calibration curve based on the peak ratio at 1378 and 1464 cm^{-1} since this ratio was found to give a better response to ethylene content than the 720 cm^{-1}/1154 cm^{-1} peak ratio for the small amount of sample collected from the GPC effluent.

Differential Scanning Calorimetry (DSC). Samples were prepared in a heated laboratory press and allowed to anneal at room temperature for 3 days prior to analysis. The sample was loaded into a Perkin-Elmer System 7 DSC instrument at +20 °C, cooled to −75 °C, and then heated to +160 °C at 20 °C/min. The DSC scan was recorded during the first melt. Heat of fusion for the PE was measured by integrating the melting curve between 70 and 140 °C using the System 7 software. Any crystallinity present in the EP segments due to high ethylene content melted at less than 70 °C and did not interfere with the determination of PE heat of fusion.

Kumagawa Extraction. A standard Kumagawa glass extractor was used. Polymers were extracted sequentially with hexane, cyclohexane, heptane, and toluene. The polymer sample was cut into small pieces and put into a wire mesh bag which was then placed in the extractor thimble. Hexane containing a small amount of antioxidant was charged to the extractor flask and refluxed at its boiling point through the thimble for 8−10 h. The system was then allowed to cool to room temperature, the hexane was removed, and the procedure was repeated with the next, higher boiling solvent charged to the flask. The extraction was carried out in a nitrogen atmosphere. Polymer was recovered by solvent evaporation and dried overnight in a vacuum oven at 60 °C.

Chain Coupling of Block Polymers with SCl_2. The polymer sample was pressed into a sheet in a mold in a heated laboratory press and a pad of the desired size was cut from the sheet. Liquid SCl_2 was placed in the bottom of a large jar and the pad was suspended from the jar lid in the vapor space above the liquid. After 18 h exposure to the SCl_2 to ensure enough time for diffusion of the vapors to the center of the specimen, the pad was vacuum-dried for 18 h at 40 °C to remove excess SCl_2. The physical properties were then measured.

Cross-Linking with EPDM. Block polymer and Vistalon 7000 were added to toluene in the desired ratio, and then the mixture was heated to 110 °C to form a solution blend. The hot solution was poured into methanol at 20 °C (methanol/toluene = 5/1 v/v) to precipitate the polymer. In all cases studied, evaporation of the supernatant to dryness indicated it contained less than 1% of the polymer. The precipitated polymer was recovered on filter paper to give a mat which was dried to constant weight in a vacuum oven at 60 °C. The mat was then exposed to SCl_2 vapor at 20 °C for 18 h to form a cross-linked network. After removal of excess SCl_2 by vacuum-drying for 18 h at 40 °C, the polymer was extracted with boiling toluene for 8 h to determine the fraction of sol.

Tensile Properties. A sheet of polymer 15 × 15 × 0.2 cm was prepared by compression molding for 15 min at 150 °C between Teflon-coated aluminum foil sheets in an aluminum mold. Dumbbell specimens die cut from the sheet were strained in tension at a crosshead speed of 12.5 cm/min. Initial jaw separation was 5 cm with about 3.3 cm of the sample undergoing most of the deformation. Engineering moduli were calculated as force at a given percent elongation divided by the original cross-sectional area of the unstrained specimen.

Results and Discussion

A. Polymer Synthesis. The general procedure for producing block polymers in a tubular reactor was to feed ethylene, catalyst and hexane diluent to the reactor inlet to grow a PE block, and then add side streams of ethylene/propylene mixtures to grow the EP block. Rapid initiation at the reactor inlet was obtained by using premixed $VCl_4/Al_2Et_3Cl_3$ catalyst, and chain transfer rates were minimized by avoiding high reaction temperatures. In solution EP polymerization, this catalyst system produces a single active site, yielding polymers with a narrow MWD and intermolecular composition distribution (CD). Due to the much higher activity of ethylene as compared to propylene, the

Table 1. Polyethylene Polymerization Results

	run 391B	run 391C	run 391D	run 391A	run 337D	run 337E	run 422A	run 422B	run 422C	run 422D	run 422E	run 422F
reactor feed[a]												
ethylene	0.4658	0.2061	0.6141	0.4523	0.1914	0.3346	0.5017	0.327	0.1672	0.1672	0.3159	0.5184
VCl_4	0.0062	0.0062	0.0062	0.0061	0.0033	0.0033	0.0084	0.0084	0.0084	0.0042	0.0042	0.0054
reactor conditions												
reactor inlet temp, °C	16	16	16	14	20	20	20	20	20	20	20	20
reactor outlet temp, °C	17	17	17	22	23	23	23	23	23	23	23	23
residence time at outlet, min	0.027	0.027	0.027	0.137	0.072	0.072	0.024	0.024	0.024	0.024	0.024	0.024
polymerization results												
ethylene conversion, %	77.8	105	77.6	103	100	105	96.3	90.9	108	94	85.2	73.9
V_0t/M_{10}, s	0.00312	0.00705	0.00237	0.01597	0.01095	0.00627	0.00348	0.00534	0.01045	0.00522	0.00277	0.00219
$M_w \times 10^{-3}$	71.1	34.2	65.4		84.3	104						
$M_n \times 10^{-3}$	29.2	16.9	31.5		36	44.5						
M_w/M_n	2.42	2.02	2.08		2.34	2.34						

[a] g/100 g of hexane.

propylene/ethylene ratio and, consequently, polymer propylene content, increases along the reactor following injection of a side stream feed. To control the intramolecular composition of the EP block, several side streams of comonomers were usually added at points along the reactor. To produce an EPDM end block, the diene, ethylidene norbornene (ENB), was added as part of the final side stream feed. The fraction of PE block in the reactor was controlled by adjusting the ratio of initial ethylene feed to side stream ethylene/propylene feed, while the length of the EPDM block was dependent on the location of the ENB feed point. Composition of the EP and EPDM block were set by the ratio of the comonomers in the feed. In this work the portion of the chain added to the block polymer between monomer feed points is referred to as a chain segment. For example, there may be several segments of different average composition in the EP block if multiple side stream feeds are used. A polymer chain that is missing one or more blocks due to termination or transfer is called a chain fragment. For a PE−EP−EPDM triblock, PE, PE−EP, EP, EP−EPDM, and EPDM are all possible chain fragments.

Polymerizations were carried out at low polymer concentration in the reactor outlet, typically 0.5−0.9 g/100 g of hexane, to avoid high viscosity and maintain turbulent flow over most of the reactor length. At these low polymer concentrations, the temperature rise along the reactor was no more than 5−7 °C with a reactor inlet temperature of 20 °C. Low polymer concentration may also assist reactor operability by slowing PE crystallization and precipitation. The $VCl_4/Al_2Et_3Cl_3$ catalyst system is very active, and reaction times of 0.1−0.2 min were sufficient to produce the desired multiblock structures.

As described in the Experimental Section, the glass tubing used for the first section of the reactor allowed visual observation of the degree of solubility of the polymer from the inlet to the second side stream addition point. The PE block formed a turbid suspension in hexane, but after injection of the side stream, the turbidity decreased substantially. The reactor effluent at 5−6% polymer concentration has the appearance of milk. After being allowed to stand about 24 h, the mixture splits into a clear supernatant and a concentrated suspension in roughly a 1:2 ratio, which then remains stable for many days with no further settling.

The synthesis studies were aimed at finding conditions that maximize the yield of the desired block polymers as compared to chain fragments. To minimize the production of PE homopolymer, it is critical to inject the first side stream of ethylene/propylene monomer as soon as the PE block reaches the desired length to limit deactivation of the catalyst attached to the growing chain. PE block growth was studied as a function of ethylene feed rate (runs 391A−C in Table 1) with a reaction quench injected into the first side stream port to give a reaction time of 0.027 min. Ethylene conversion was high in all cases (see Figure 1) but tended to decrease with increasing monomer feed rate. Combining the results from run 391 with the other data in Table 1 for PE block formation as a function of catalyst and ethylene feed rates and residence time indicates that conversion can be correlated reasonably well (see Figure 2) with the parameter V_0t/M_{10} where V_0 and M_{10} are the initial catalyst and monomer concentrations and t is the reaction time (conversions greater than 100% in Figure 2 represent inaccuracies in the feed and polymerization rate measurements that go into the reactor material balance calculations). An increase in conversion with increases in catalyst feed rate and reaction time is expected, but the inverse dependence of conversion on ethylene concentration suggests that ethylene must be participating in a mechanism that reduces active catalyst concentration. We cannot determine from the available data whether this mechanism is rooted in chemical effects or physical effects related to polymer insolubility.

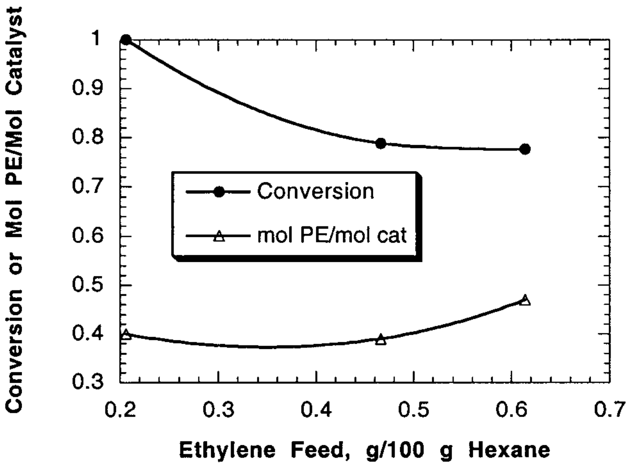

Figure 1. Ethylene homopolymerization results.

For di- and triblock polymers, the data in Figure 2 were used to set PE polymerization conditions to obtain ethylene conversions of 80−100%, so that the amount of PE block in the final polymer could be anticipated from the ethylene feed rate to the reactor inlet. PE block content was measured by DSC. PE homopolymers made

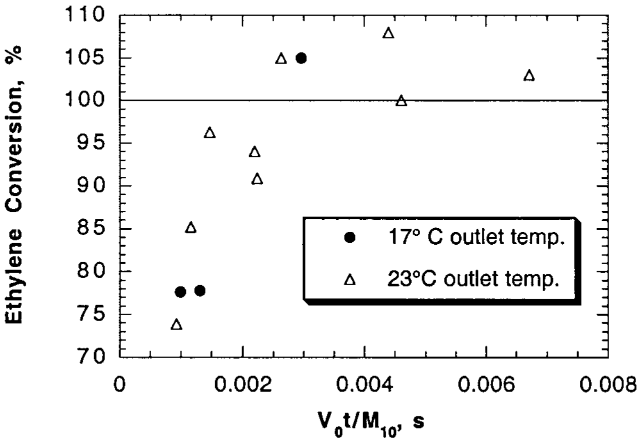

Figure 2. Ethylene conversion correlation.

in a number of polymerizations had a heat of fusion over the melting range from 70 to 140 °C that averaged 181 J/g. Assuming that in multiblock polymers the heat of fusion of the PE block is unaffected by the presence of the amorphous block, then the fraction of PE block can be calculated by dividing the heat of fusion from 70 to 140 °C by 181 J/g. At reaction conditions where V_0t/M_{10} exceeded 0.0018 (see Figure 2) and essentially all of the initial ethylene feed reacted, the fraction of PE block calculated from DSC and from dividing the initial ethylene feed rate by total polymerization rate were in close agreement. In general, the PE block of the polymers produced in this study was less than 50% of the total polymer.

To obtain high yields of block polymer, it is also important that chain initiation is complete in the PE section of the reactor and PE MWD is narrow. The moles of polymer produced per mole of vanadium fed, N_v, is an indicator of chain initiation and termination kinetics. In the absence of chain transfer and with 100% of the catalyst initiated, N_v should equal 1. However, as shown in Figure 1, N_v is much less than 1 primarily because of deactivation of a portion of the catalyst prior to chain initiation. Most of this deactivation occurs in the catalyst premixing step since it is well-known for soluble vanadium catalysts that premixing causes a loss in catalyst activity as compared to combining the catalyst components in the presence of monomer. N_v is fairly constant for the three runs, and the average value of 0.42 indicates that a maximum of 42% of the catalyst feed to the premixer enters the reactor as active sites. To get the actual percentage, N_v has to be corrected for the contribution of polymer produced by chain transfer to the total moles of polymer produced. M_w/M_n (see Table 1) for these PE homopolymers ranges from 2.0 to 2.4 indicating that transfer or some other MWD broadening process has occurred.

In EP solution polymerization in the same reactor with the same catalyst system, the moles of polymer generated per mole of catalyst ranged from 0.35 to 0.62 in nine experiments and averaged 0.50. This is not appreciably different from the value for PE homopolymerization. However, M_w/M_n for the EP copolymers varied from 1.28 to 1.65 as compared to 2.0 or greater for the PE. The reason the PE MWD is so much broader than that of the EP is uncertain. High chain transfer rates in this polymerization usually are related to high propylene concentrations, and we feel that catalyst deactivation cannot account for the observed result based on the kinetic modeling work done in the prior study by Ver Strate et al.[10] Possible explanations for the broadened MWD in the PE reactor section are an unexpected chain transfer reaction, physical effects arising from polymer crystallization and precipitation, and a very short-lived second catalyst species. Georgiadis and Manley[16] studied ethylene polymerization with a soluble $VOCl_3-AlEt_2Cl$ catalyst and found that two different kinds of PE particles were produced—the majority of particles had a fibrillar shish kebab structure, but much denser particles with a granular texture were also present. The different particle morphologies were correlated with the presence of a soluble and colloidal catalyst species. Conceivably, the $VCl_4-Al_2Cl_3Et_3$ catalyst also produces a colloidal species, which is responsible for the PE chain fragments, and a soluble species of higher activity, which forms the block copolymer.

Table 2. Material Balance Calculations for Polymer Structure

Overall Polymerization Results

	PE−EP diblock		PE−EP−EPDM triblock	
	run 324A	run 324C	run 320B	run 320A
polymerization rate, g/h	365	655	387	432
polymer composition, wt %				
ethylene	66.5	64.4	71.6	71.3
ENB	0	0	0	0.18
$M_w \times 10^{-3}$	123	189	189	206
$M_n \times 10^{-3}$	74.5	114	108	108
M_w/M_n	1.73	1.7	1.67	1.9
moles of polymer/mole of VCl_4	0.394	0.462	0.384	0.429
monomer conversion, %				
ethylene	81	78.4	65	72.1
propylene	8.4	11.7	5.7	6.4
ENB				9.7

Polymer Segment Characterization

	run 324C			run 320A		
segment	PE	EP 1	EP 2	PE	EP	EPDM
% of polymer	9.7	46	44.3	20.9	70.8	10.4
composition, wt %						
ethylene	100	59.6	61.8	100	62.9	68.7
ENB	0	0	0	0	0	1.7
conversions, %						
ethylene	86.4	77.9	59.5	60.1	56.8	20.8
propylene		8.4	6		5.69	0.77
ENB						9.7

Di- and triblock polymerizations were typically carried out with two or three ethylene/propylene side stream feeds to limit the composition variation in the EP block. For producing triblocks, ethylidene norbornene (ENB) was added as part of the final reactor feed stream. By measurement of the polymerization rate and average polymer properties (e.g., composition and molecular weight) as a function of reaction time, the amorphous polymer segment produced in each section of the reactor can be characterized. An example of multiblock polymer structure analysis for a PE−EP diblock is given in Table 2. In run 324A two ethylene/propylene side streams were added at residence times of 0.024 and 0.11 minutes and the reaction was quenched at 0.147 min. Run 324C was identical to run 324A, except a third side stream was added at 0.147 min and the reaction was quenched at 0.203 min. The feed rates for these two runs are compared in Figure 3 (detailed

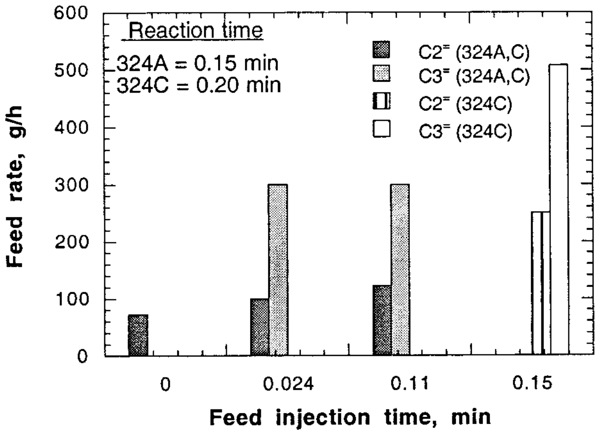

Figure 3. Run 324 feed rates.

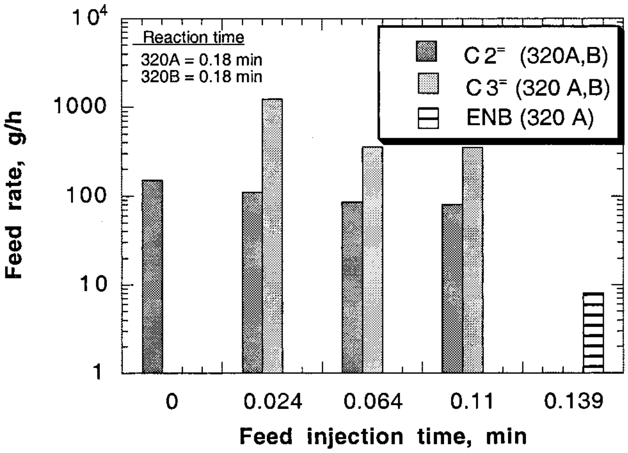

Figure 4. Run 320 feed rates.

polymerization data for these runs and the other runs discussed in this paper can be found in the Supporting Information).The difference in reaction rates between runs 324A and 324C represents the additional amount of EP polymer produced by adding a third side stream feed. DSC analysis indicated the fraction of PE block is 9.7% for run 324C. In run 324A, the polymerization rate in the PE section of the reactor will be the same; however, since less EP was made than in run 324C, the PE fraction will be increased by the ratio of polymerization rates. If material balance calculations are carried out based on compositions, feed rates, and reaction rates, the composition of EP segment and the monomer conversions in the section of the reactor with reaction time between 0.147 and 0.203 can be determined. As shown by the results for 324C in Table 2, the final EP segment (EP 2) is present in about the same amount and has about the same composition as the preceding EP segment (EP 1). Monomer conversions were less in the final section of the reactor due to the decrease in catalyst concentration with increasing reaction time.

A similar analysis for a triblock polymer gives the characteristics of the EPDM block. In run 320B (see Figure 4), three side streams were used to produce an PE−EP diblock at a total reaction time of 0.139 min. In run 320A, an ENB solution in hexane was added at this point and the reaction time was extended to 0.176 min. The difference in reaction rates of 45 g/h represents the amount of EPDM added to the diblock. Once again, material balance calculations can be used for each section of the reactor to determine the polymer composition and monomer conversion, and the results are shown in Table 2. The triblock polymer, 320A, contains 0.18 wt % ENB on average, but the EPDM block contains 1.7% ENB and comprises 10.4% of the polymer. As shown in Table 2, in run 320A the monomer conversions are low in the EPDM section of the reactor. This was due to the relatively low concentrations of ethylene, propylene, and active catalyst in the reactor at the point of ENB addition. The EPDM block polymerization rate can be increased by feeding additional ethylene and propylene with the ENB.

In these polymerizations, N_v is about 0.4 mol chains per mole of vanadium (see Table 2), the same result obtained for ethylene homopolymerization (see Figure 1), indicating that the addition of ethylene and propylene feeds did not grossly increase the rates of chain transfer reactions. However, for both runs 320 and 324 there was a slight increase in N_v when residence time was extended. We believe this is due to an increased rate of propylene chain transfer reactions near the end of the reactor where temperature and propylene/ethylene concentration ratio are the highest. For example, comparing runs 324A and 324C shows that increasing the amount of polymer made by 84.5% increases M_n by only 53%, rather than the 84.5% expected for a true living polymerization. Finally, we note that M_w/M_n for the polymers in Table 2 is 1.7−1.9 as compared to 2.0 or more for the PE block alone. Thus adding EP to the PE causes the MWD to narrow. Clearly, the mechanism leading to broad MWD in the PE section of the reactor is largely absent in the EP section. MWD narrows because polymerization in the EP section is primarily by chain extension of the living PE blocks, and the dead PE fragments are reduced as a fraction of the chain population by the additional polymerization.

B. Polymer Characterization. The characterization studies focused on determining the amount of the desired block polymer product as a function of the reaction conditions. Solvent extraction, which can readily separate amorphous from crystalline polymers, was used to measure the amount of polymer formed by chain transfer in the EP/EPDM section of the reactor. In diblock polymerization, the expected products are PE, PE−EP, and EP. The insoluble polymer after extraction of the EP chain fragment is PE and PE−EP. The fraction of insoluble polymer sets an upper limit on the diblock polymer yield, and approximates this yield if the amount PE fragment is small. Quantitative separation of the PE fragment from PE−EP is difficult. Fractional crystallization or dissolution (TREF) may be suitable, but these methods were not investigated in this study. As discussed below, GPC−FTIR can provide a rough estimate of the amount of PE fragment. Separation of a PE−EP−EPDM triblock into components is more complicated than for the diblock since three additional chain fragments, PE−EP (previously the desired final product), EP−EPDM, and EPDM, are produced. We used the following procedure for triblock fractionation:

1. Extract a triblock polymer (A) sample with boiling hexane to remove (EP + EPDM) fragments (B).

2. Cross-link a second triblock polymer (A) sample to form a network incorporating all of the EPDM containing chains. Extract the network with boiling hexane to remove EP fragments (C) and then extract with boiling toluene to remove (PE + PE−EP) fragments (D).

Table 3. Solvent Fractionation Results

			composition, wt %					
run	fraction	% dissolved	PE block	ethylene	ENB	PE block, T_m, °C	$M_n \times 10^{-3}$	M_w/M_n
341A	whole polym	0	31.4	68.6	0.28	130.9	84	1.75
	hexane	15.9	3.0	58.7		124.5	58.6	2.04
	cyclohexane	10.7	29.7	68.3	0.32	127.7		
	heptane	5.6	27.6	66.3	0.27	128.6		
	toluene	67.8	32.2	70.5	0.32	129.0		
347B	whole polym	0.0	38.2	71.3	0.18	131.2	104.0	1.91
	hexane	12.0	0.0	49.3	0.48		64.2	2.06
	cyclohexane	1.2	0.7			109.2		
	heptane	4.7	6.0			124.0		
	toluene	82.1	40.0	78.7	0.14	130.5		
346C	whole polym	0.0	48.6	74.3	0.26	132.3	112.0	1.85
	hexane	5.9	0.0	47.1	0.68		53.5	1.99
	cyclohexane	1.8	0.6			111.9		
	heptane	1.4						
	toluene	90.8	49.0	79.2	0.14	131.8		

The amount of each species can then be calculated from

$$\text{PE-EP-EPDM} = (A) - (B) - (D)$$

$$(\text{PE} + \text{PE-EP}) = (D)$$

$$\text{EP} = (C)$$

$$\text{EPDM} = (B) - (C)$$

Characterization of the amorphous fragments in three triblock polymers by sequential extraction with a series of solvents of increasing boiling point gave the results shown in Table 3. The polymers differ primarily in the percentage of PE block, which ranges from 31 to 49% and was varied by increasing the inlet ethylene feed rate while decreasing the feed rate of comonomers to the side streams. For sample 341A, which has the lowest molecular weight of the set, the hexane fraction is essentially EP and EPDM, with a small amount of diblock polymer present, as calculated from the heat of fusion at 70–140 °C. The extracted diblock presumably has a very low molecular weight. The other three fractions are all similar in composition and clearly represent polymer containing a PE block. Thus for sample 341A, about 15% of the polymer was formed by chain transfer in the EP/EPDM section of the reactor. For runs 347B and 346C, almost all of the block polymer is in the toluene-soluble fraction. The hexane fraction contains no PE segments, and minor amounts of PE are present in the cyclohexane and heptane fractions. Thus, the EP and EPDM fragments are in the hexane/heptane soluble fractions which totaled 17.9 and 9.2% of the polymer in runs 347B and 346C, respectively. Solvent extraction of additional polymers made over a range of polymerization conditions gave similar results for the amount of amorphous fragment. Depending on the details of the feed rates and feed locations, 10–20% of the total polymer does not contain a PE block.

GPC/FTIR analysis provides additional information about the nature of the polymerization process. Figures 5 and 6 show the polymer composition as a function of molecular weight for the hexane insoluble and soluble fractions of a PE–EP diblock polymer with the characteristics given in Table 4. For the insoluble fraction (Figure 5) the compositions can be classified into three zones: (1) region I up to log MW = 4.2 in which the polymer composition is essentially polyethylene; (2) region II from log MW = 4.2 to 4.7 in which the ethylene content of the polymer decreases to a roughly constant value; (3) region III of constant composition at log MW greater than 4.7.

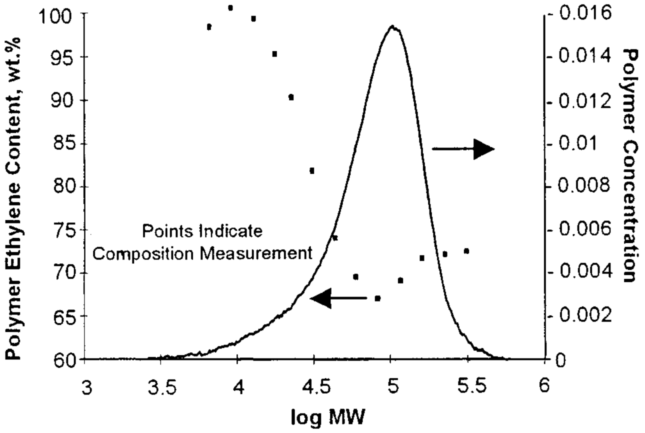

Figure 5. GPC/FTIR analysis for insoluble fraction.

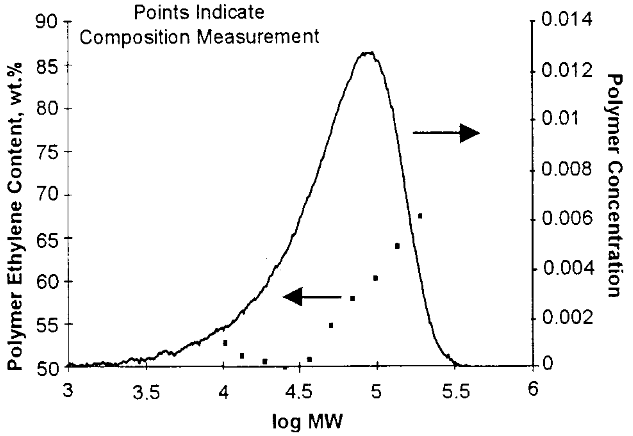

Figure 6. GPC/FTIR analysis for soluble fraction.

We ascribe the first region to polyethylene formed by chain termination in the PE block section of the reactor, the second region to block copolymer that terminated early in the EP section of the reactor and so did not attain full chain growth, and the final region to block copolymer that grew over essentially the entire reactor length. If analytical expressions were available for the MWD of each of these polymer fractions, it would be possible to deconvolute the MW curve into three separate MWD's and quantify the amount of each fraction present. However, such expressions are lacking.

Table 4. Characteristics of Block Polymer Shown in Figures 5 and 6

	whole polymer	hexane soluble	hexane insoluble
% of polymer	100	13.5	86.5
$M_n \times 10^{-3}$	67.8	57.2	(69.8)[a]
$M_w \times 10^{-3}$	96.4	88.8	
M_w/M_n	1.42	1.55	
composition, wt %			
PE block	19.8		(22.9)[a]
ethylene	64.9	55.6	67
ethylene in EP segment	56.2		

[a] Calculated by material balance.

For the insoluble fraction, the area under the MW curve in region I is clearly due to PE fragments. Since some of this material undoubtedly exists at higher MW also, this area sets a lower limit on the amount present. M_n for the PE block should be roughly equal to the fraction of PE in the block polymer times M_n for the block polymer or $0.229 \times 69\,800 = 16\,000$. To get a better estimate of the fraction of PE fragment, we start by assuming it has an average molecular weight similar to that of the PE block. The upper bound of region I, log MW = 4.2 (MW = 15 800), would then be in the vicinity of the peak of the MWD for the PE fragment. Finally, if this MWD is symmetrical, twice the area in region I would be a reasonable approximation for the total amount of PE fragment. Region I represents 4.2% of the total polymer which gives an estimate of 8.4% for the quantity of PE homopolymer in the insoluble fraction. Thus the overall composition of the whole polymer in Table 4 is estimated to be 13.5% EP fragment, 7.3% PE fragment, and 79.2% of the desired diblock polymer. At the point where the first side stream feed entered the reactor, 63% of the PE was living chains and 37% was terminated PE fragment.

The soluble fraction also exhibits a composition distribution across the MWD, as shown in Figure 6, with the ethylene content of the polymer decreasing as MW decreases. This result is consistent with the general trend toward increasing propylene/ethylene monomer ratio along the EP section of the reactor, although the increase is not monotonic due to the side stream feed injections. Thus non-PE-containing chains initiated following a chain transfer event early in the EP section will have a higher molecular weight and ethylene content than chains that begin toward the end of the reactor in a region of high propylene concentration and have only a short time to grow. Also note that the MWD is skewed toward low MW. This is believed to be a consequence of chain transfer rates increasing due to rising temperature and propylene/ethylene monomer ratio along the reactor length.

The yield of PE−EP−EPDM triblock was determined by exposing the polymer to sulfur dichloride to cross-link the chains followed by solvent extraction, as described in the Experimental Section. The success of this technique hinges on incorporating all of the EPDM blocks into a cross-linked network. This does not occur with pure triblock polymer since ENB content is deliberately kept low to provide a processible TPE after chain coupling, and a large fraction remains as sol after treatment with SCl_2. When the triblock polymers are blended with an EPDM of higher ENB content, all of chains containing ENB could be cross-linked into a gel. Experiments with varying ratios of triblock polymer to Vistalon 7000 (70% ethylene, 4.9% ENB) indicated that the soluble fraction after cross-linking reached a constant level for blend ratios less than 1/1. Runs 338B and 354B were made at typical triblock polymerization conditions. In run 338B, the ENB was added later (0.151 min vs 0.107 min) and at 53% of the amount used in run 354B (see Figures 7 and 8). Thus, run 338B should contain a lower fraction of EPDM block. Both polymers were extracted with boiling hexane to measure the amount of EP plus EPDM chain fragments, and the whole polymers were also extracted with boiling toluene after cocuring with V-7000 in a 1/4 triblock/V-7000 ratio to measure the amount of PE, PE−EP, and EP fragments. The results of the analysis are given in Table 5 along with the characteristics of the whole polymers and the fractions.

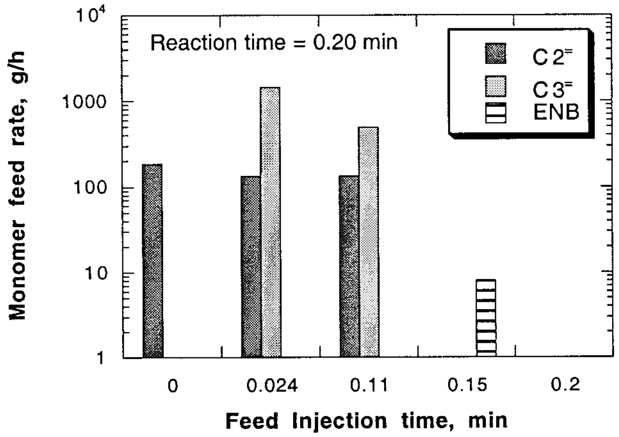

Figure 7. Run 338B feed rates.

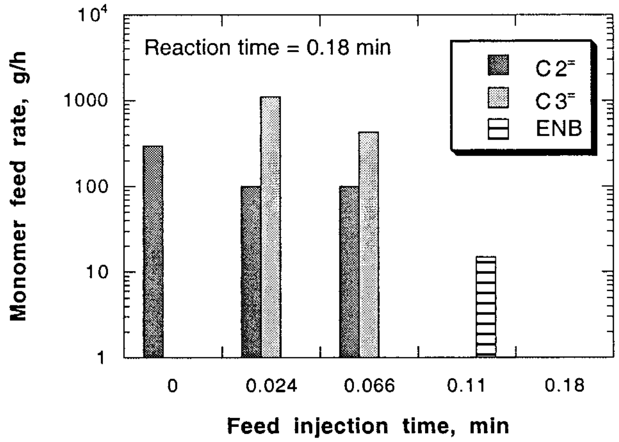

Figure 8. Run 354B feed rates.

For run 338B, 20.6% of the polymer is EP and EPDM free of PE, (hexane/heptane soluble fraction precure) while 15.3% of the polymer is PE, PE−EP, and EP (toluene solubles postcure). The EP fragments appear in both solubles fraction, because, unfortunately, a hexane extraction of the postcured sample to measure the amount of EP was omitted. Adding these two fractions together indicates that the triblock yield is greater than 64% since the EP was counted twice. For run 354B, in which the ENB was added earlier and in greater amount, the toluene solubles after curing decreased slightly to 12.9%, and the precure solubles fraction in this run was 15.7%. Thus for this run the triblock yield was at least 71.4%. Eleven different polymers made over a range of ENB feed rates and addition times were analyzed in this fashion, and the amount of toluene solubles after curing varied from 10

Table 5. Extraction of Cured Polymer To Determine the Fraction with ENB

	run 338B			run 354B		
	whole polymer	hexane soluble precure	toluene soluble postcure	whole polymer	hexane soluble precure	toluene soluble postcure
% of polymer	100	20.6	15.3	100	15.7	12.9
$M_w \times 10^{-3}$	217					
$M_n \times 10^{-3}$	91.4					
M_w/M_n	1.98					
composition, wt %						
PE block	35.2	0		49.7	0	
ethylene	67.6	47.1		74.9	51.9	
ethylene in EP segment	50			49.9		
ENB	0.2	0.45		0.56	1.43	

to 30% depending on the synthesis conditions. Under optimal conditions, triblock yields in excess of 80% are feasible.

C. Polymerization Kinetics. Product design and reactor optimization for a tubular reactor with multiple side feeds are complicated by the large number of reactor parameters that can be independently varied. These include the number of side streams, the ethylene, propylene, and ENB content of the side streams, and the residence time at which the side stream is injected. Catalyst feed rate and reactor temperature also have a very large influence on reactor performance. A kinetic modeling approach was adopted to correlate the data from this study so that the effect of reactor conditions on product properties could be predicted. Because three monomers are involved, a full kinetic scheme for the polymerization, including all possible propagation, termination, and transfer reactions common to Z–N catalysis, would require 20–30 reaction steps. Due to the large number of reactions and the fact that they all occur in parallel, determining rate constants for a mechanism of this complexity was not feasible.

Consequently, a pragmatic approach was taken to develop a model that could predict the effect of reactor conditions on product properties with a high degree of reliability, but that was not necessarily correct in all of the mechanistic details. Model construction involved the following approximations.

1. The chain initiation rate was assumed to be much faster than chain propagation rates. The validity of this approximation is supported by the very narrow MWD polymers produced in the previous work by Ver Strate et al.[10]

2. Propagation reactions involving addition of ENB to an ENB ended chain, ENB to a propylene ended chain, and propylene to an ENB ended chain were assumed to be unimportant due to steric inhibition and were omitted.

3. Catalyst deactivation was assumed to occur by a spontaneous first-order decay and by reaction with propylene.

4. Chain transfer was assumed to occur only by monomer transfer with propylene.

5. Catalyst deactivation and chain transfer rate constants were assumed to be independent of the last monomer added to the chain to further reduce the number of rate constants in the model.

The resulting kinetic model is shown in Table 6. We did not try to model the details of the polymerization in the PE section of the reactor due to lack of a proven mechanism which would account for M_w/M_n equal to 2.0 or more and the unusual dependence of conversion on ethylene concentration mentioned earlier. The only reactions in Table 6 that occur in the PE section of the reactor are chain propagation and catalyst decay. This is sufficient to account for PE polymerization rate in the block copolymerization experiments because reaction conditions were typically adjusted to give a 90–100% conversion of the initial ethylene feed. Thus, for modeling purposes, k_{11} was set large enough to give this conversion level over the range of conditions investigated. As a result, the PE polymerization rate may not be accurately predicted at lower conversions, nor is the PE MWD calculated correctly, which has consequences for the ability of the model to predict block polymer MWD, as discussed below.

Table 6. Polymerization Mechanism[a]

mechanism	rate const at 25 °C, mol/(L h)
Propagation	
$P_i + M_1 \rightarrow P_{i+1}$	$k_{11} = 0.490 \times 10^{10}$
$Q_i + M_1 \rightarrow P_{i+1}$	$k_{21} = 0.123 \times 10^{8}$
$R_i + M_1 \rightarrow P_{i+1}$	$k_{31} = 0.478 \times 10^{10}$
$P_i + M_2 \rightarrow Q_{i+1}$	$k_{12} = 0.212 \times 10^{9}$
$Q_i + M_2 \rightarrow Q_{i+1}$	$k_{22} = 0.681 \times 10^{6}$
$P_i + M_3 \rightarrow R_{i+1}$	$k_{13} = 0.478 \times 10^{8}$
Catalyst Deactivation with Monomer	
$P_i, Q_i, R_i + M_2 \rightarrow D_i$	$k_m = 0.202 \times 10^{3}$
Chain Transfer with Monomer	
$P_i, Q_i, R_i + M_2 \rightarrow D_i + P_1, R_1, Q_1$	$k_{tr} = 0.782 \times 10^{3}$
Spontaneous Catalyst Deactivation	
$P_i, Q_i, R_i \rightarrow D_i$	$k_t = 0.179 \times 10^{5}$ [b]

[a] Nomenclature: M_1 = ethylene; M_2 = propylene; M_3 = ENB; P_i = growing chain with M_1 as last added monomer; Q_i = growing chain with M_2 as last added monomer; R_i = growing chain with M_3 as last added monomer; D_i = terminated chain; k = rate constant. [b] Units: h^{-1}.

The rate equations for the mechanism lead to a set of simultaneous, ordinary differential equations (ODE) describing monomer concentration, growing and dead chain concentration, and MWD moments as a function of time which can be derived by standard methods.[17] These equations can be solved by any of a number of computer-based ODE algorithms to predict polymerization rate, polymer composition, molecular weight, and MWD as a function of reaction conditions. However, the use of multiple side stream feeds is a complication because the integrator must be stopped, initial conditions readjusted, and then integration restarted each time a side stream feed is added. Thus we adopted the numerical algorithm described in the previous study[10] in which the tubular reactor is modeled as a train of 400 continuous flow stirred tank reactors (CFSTR) in series or, in other words, by a series of differential elements. The algebraic material balance equations for a CFSTR are solved from stage to stage to track the course of the polymerization over the length of the reactor.

Determination of rate constants requires knowledge of the catalyst concentration at the reactor inlet. However, the active catalyst concentration for Z–N polymerization is a matter of some uncertainty since it cannot easily be measured experimentally and must be inferred from the polymerization data. For nonpremixed, soluble $VCl_4/Al_2Cl_3Et_3$ catalysts in ethylene/propylene solution polymerization, approximately 1 mol of polymer is produced per mole of vanadium fed to the reactor when chain transfer is minimized. This is an indication that all of the vanadium initiates a growing chain. As shown earlier, catalysts premixed at optimal conditions generate about 0.4 mol of copolymer per mole of vanadium, which puts an upper limit of 40% on the amount of catalyst feed that becomes active. The actual amount of active catalyst will be less than 40% since the 0.4 value includes polymer formed in chain transfer reactions. From the analysis of the soluble and insoluble fractions for various polymers produced in this study, as shown for example by the data in Table 4, the moles of block polymer formed per mole of catalyst fed to the reactor is estimated to be in the range 0.30–0.37. The lower end of this range, or 30% of the catalyst fed, was chosen for calculating the catalyst concentration at the reactor inlet.

Polymerization rate constants were estimated by manually adjusting a starting set of values until there was reasonably good agreement between experimental and calculated polymer composition, molecular weight, and polymerization rate. The data set used to fit the rate constants included polymerization runs that varied in the feed rates of the monomers and catalyst, overall residence time, and the time of side stream injection. The rate constants at an average reactor temperature of 25 °C determined by this procedure are given in Table 6, and as shown in Figure 9, the predicted composition is within 5% of measured values and the predicted M_n and polymerization rate are within 10%. The model constants were tuned to predict M_n which causes M_w/M_n to be underpredicted by 0.3–0.4 since the PE block is calculated to have a M_w/M_n equal to about 1.0 when it is actually closer to 2.0. Although the absolute values differ, trends in the calculated M_w/M_n do follow trends in the measured values. Since a statistical fitting method was not used to determine the rate constants in Table 6, other sets of values likely exist that can provide an equivalent fit to the data. However, we do feel that the ratios of the constants are indicative of relative rates for the various polymerization reactions.

The polymerization model is useful for calculating overall reactor performance and polymer properties at the reactor outlet, but equally important it allows prediction of polymer properties along the length of the reactor. For example, in run 324, which was discussed in detail above (see Table 2), the calculated incremental and cumulative polymer composition are shown as a function of residence time in the lower part of Figure 10. (Incremental composition is the polymer composition added to the chain in one of the CFSTR elements. For a true differential element this would be the instantaneous composition.) Following the formation of the PE block there is step drop in incremental polymer ethylene content upon addition of the first side stream feed. Ethylene content continues to fall with distance along the reactor because the higher reactivity of ethylene relative to propylene enriches the unreacted propylene concentration. When the second side stream feed is added, polymer ethylene content rises initially and then falls again as ethylene is consumed. This pattern is

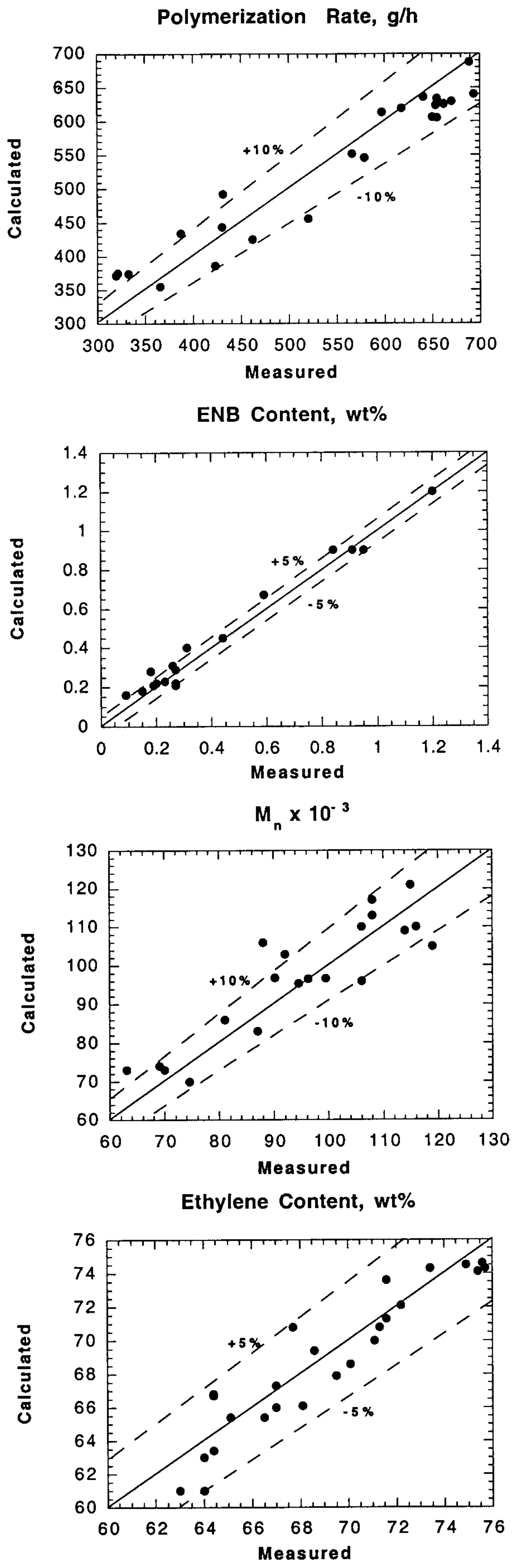

Figure 9. Kinetic model results.

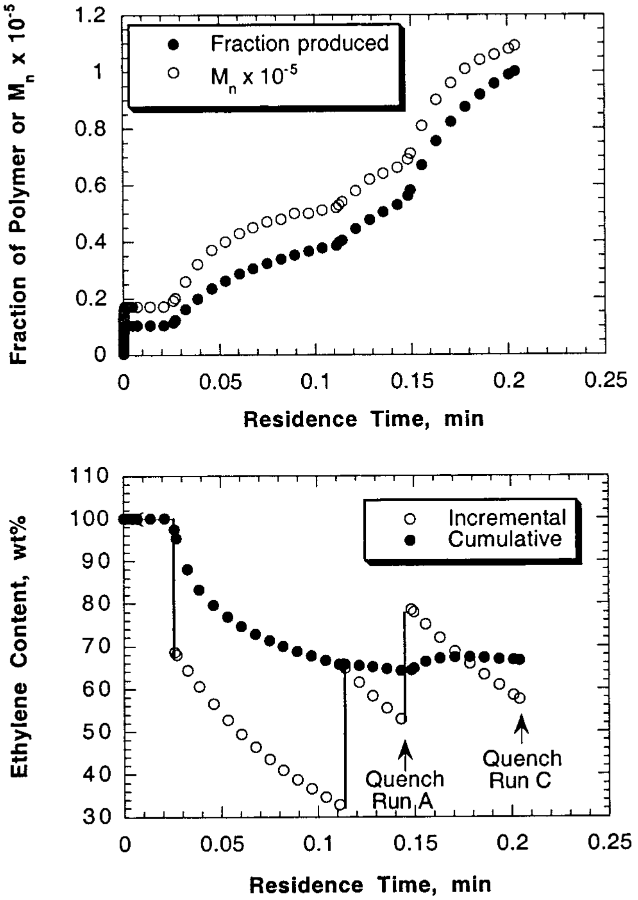

Figure 10. Calculated results for run 324.

repeated when the third side stream is added in run 324C. The average composition of EP segment produced following the first, second, and third side stream feed rises in that order due to the ethylene/propylene ratios in the feed. The third side stream composition causes a distinct increase in the cumulative (average) ethylene content of the polymer, and a marked change in polymer structure as compared to only two feeds. By adjusting the number and composition of the side stream feeds and the timing of their addition it is clear that any number of intramolecular composition distributions can be constructed in the EP block.

The upper part of Figure 10 shows the fraction of total polymer produced at a given residence time and the corresponding cumulative M_n. Polymerization rate, which is the slope of the former curve, is high when a side stream feed is introduced and then declines toward zero due to the depletion of ethylene. To minimize chain transfer involving propylene, it is important to add a new side stream before the ethylene/propylene monomer ratio in the previous reactor section gets too low. Thus these calculations also indicate optimum feed locations for minimizing MWD breadth. The shape of the M_n curve duplicates the shape of the polymer fraction curve since polymerization results primarily in chain extension. Consequently, in this polymerization system, molecular weight is proportional to the ratio of polymer produced to the number of chains initiated (i.e., the catalyst feed rate).

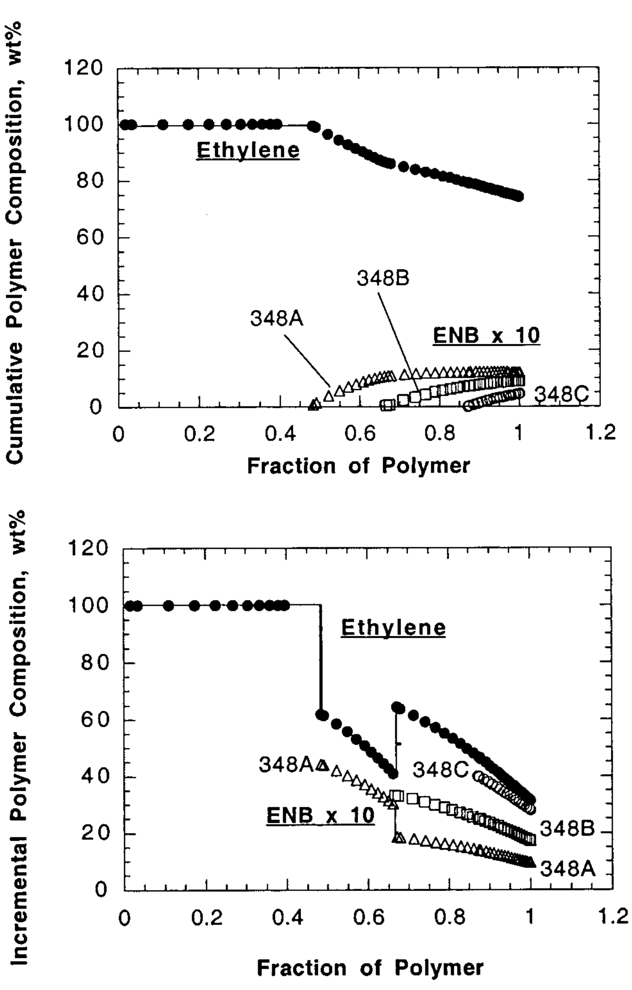

Figure 11. Calculated results for run 348.

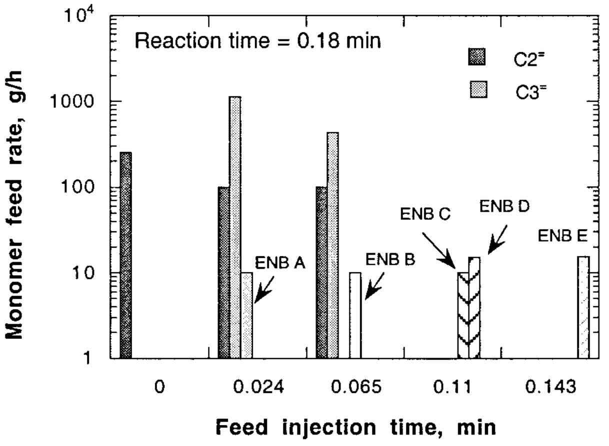

Figure 12. Run 348 feed rates.

Similar calculations were carried out to estimate the details of the ENB composition distribution for the polymers made in run 348 (see Figure 12), which are extensively characterized later in this paper. Two ethylene/propylene side stream feeds and a single ENB side stream feed were used in this run. Runs 348A, 348B, and 348C compare the effect of feeding the ENB with the first E/P side stream (run A), the second E/P side stream (run B) and finally in a third side stream with no ethylene and propylene (run C). As shown by the results in the upper part of Figure 11, the fraction of polymer containing ENB decreases from 50% to 15% as the ENB feed point is moved downstream, and the cumulative ENB content of the polymer also decreases in view of the reduced amount of EPDM block. However, as shown in the lower half of the figure, the ENB content of the EPDM block increases by moving the ENB feed further downstream since this raises the ENB monomer concentration relative to the ethylene and propylene. As mentioned later, when these polymers were reacted with a chain coupling agent, runs 348A and 348B formed a cross-linked network, but run 348C did not. Thus calculations of this type are also useful for determining the chain structures most likely to give target performance after chain coupling.

D. Polymer Properties. Chain coupling of PE−EP−EPDM triblocks at the residual olefinic unsaturation in the EPDM produces a multiarmed analogue of a star-branched polymer. The central part of the coupled polymer will consist of an amorphous, elastic, EPDM core while the PE−EP chain segments with crystalline PE end blocks will extend outward and be free to cocrystallize with other PE blocks. The number of branches emanating from the central nodule will of course depend on the fraction of the polymer that is EPDM, the diene content of the EPDM, and the fraction of olefin groups reacted.

It was expected that there would be an optimum range of EPDM chain compositions giving good TPE properties and a processable polymer after chain coupling. If the EPDM block is too long, chain coupling will lead to a thermoset, cross-linked network. On the other hand, if it is too short, or if the diene content is too low, there may be a high fraction of chains that do not couple, and TPE properties will suffer. Also, EPDM block length and diene content are related by the polymerization kinetics. If short reaction times are used to restrict the fraction of EPDM, it is difficult to incorporate a high diene level. To explore the requirements for producing the best chain structure, a series of polymerizations were carried out at constant polymerization conditions except that the ENB injection point was moved to progressively longer times to vary the EPDM block length and ENB content.

Reactor feed rates for this series of runs are shown in Figure 12. In runs 348A−C the ENB feed rate was held constant at 10 g/h, and the ENB feed point was moved down the reactor to shorten the EPDM block length. Run D was the same as run C except the ENB feed rate was raised to 15 g/h. In run E, the ENB feed rate was maintained at 15 g/h and the feed point was again shifted further down the reactor. The polymers resulting from these polymerizations, as shown in Table 7, are very similar in characteristics except for the ENB content and fraction of EPDM block which gets progressively smaller as the ENB injection point is moved closer to the reactor outlet. The fraction of EPDM was not measured directly, but estimated from simulations with the kinetic model shown in Figure 11. After coupling by exposure to sulfur dichloride, simple engineering properties were measured at 20 °C, with the results shown in Table 7.

Coupled polymers 348A and 348B had a much lower extension at break than the other samples and could not be properly mixed with carbon black and oil. Clearly, the length of the EPDM block was sufficient to form a cross-linked network. Polymers 348C, 348D, and 348E could be compounded with carbon black and oil after chain coupling. For these three polymers, the elongation at break decreases and 100% modulus increases with an increase in either ENB content or EPDM fraction, as would be expected, and they have attractive TPE properties, with tensile strengths at 20 °C of 12−16 MPa. The tension set for all of the samples in Table 7 was low and varied between 6.3 and 9.4%. Although tensile strength was not measured on the uncoupled polymers for these particular samples, results for similar polymers indicates that chain coupling raises the tensile strength by a factor of 2−4, depending on the details of polymer structure. Thus we conclude that triblock polymers with 40−45% PE block should contain 5−15% EPDM block for the optimum properties. These polymers have superior properties when compared to statistical EP copolymers of the same average ethylene content.

Table 7. Effect of ENB Feed Point on Polymer Composition

	run 348A	run 348B	run 348C	run 348D	run 348E
ENB feed point, % of total reaction time	13.6	37.2	59.9	59.9	80.8
Mooney viscosity (1 + 4, 150 °C)	53.3	46.2	42.5	44.4	43.1
$M_w \times 10^{-3}$		208	202	196	162
$M_n \times 10^{-3}$		90.2	96.2	99.4	94.5
M_w/M_n		2.04	1.86	2.01	1.91
composition, wt %					
PE block	44.4	44	44.6	43.4	43.4
ethylene	75.4	75.7	75.6	74.9	73.4
ethylene in EP segment	55.8	56.6	56	55.7	53
ENB	1.2	0.91	0.44	0.59	0.27
EPDM block (est)	54.6	35.6	13.7	13.7	5.2
ENB in EPDM block (est)	2.2	2.6	3.2	4.3	2.1
modulus, 100%	broke	7.6	5.35	5.6	4.8
tensile strength, MPa	5.4	12.4	15.9	15.2	12.3
elongation at break, %	36	190	650	580	760
tension set,[a] %	6.3	6.3	9.4	9.4	9.4

[a] Set measured after 10 min at 100% elongation followed by 10 min of relaxation.

The coupled polymer from run 348E was extracted with hot toluene to determine the extent of network formation, and 59% of the polymer was soluble. M_w for the soluble fraction was 297 000 by GPC−LALLS analysis as compared to 162 000 for the initial, uncoupled polymer. Despite the presence of a relatively large insoluble fraction, this polymer was reprocessible after chain coupling, as mentioned above.

Chain coupling with sulfur dichloride is a useful laboratory technique, but more standard cure systems are required for commercial products. A number of samples were coupled with a conventional sulfur accelerator cure system by banding the rubber on a heated two roll mill at 140 °C, milling in the curatives over a period of 4 min, and then forming compression molded pads from the compounded product. The pads were cured in an electric press for 20 min at 160 °C, and dumbbell specimens were cut for the measurement of tensile properties. Table 8 gives the properties of three typical triblock polymers with about 40% PE block and Mooney viscosity ranging from 24 to 78. For sample 361B, the tensile strength increased by a factor of 3 after chain coupling. The polymer remained reprocessible, and the cured pad could be repressed in a new pad with the same physical properties. Sample 365C also exhibited the same physical properties after the chain coupled polymer was reprocessed into a new pad. For samples 365C and 367A, tensile properties measured at 20 and 60 °C indicates that tensile strength decreases as the temperature is raised due to a loss of crystallinity, but enough strength is retained at 60 °C temperature to still provide useful TPE properties. In comparison, an uncured random ethylene/propylene copolymer of similar average ethylene content (77%) has comparable tensile

Table 8. Properties of Sulfur-Cured Polymers

		run 361B			run 365C		run 367A	
polymer characteristics								
Mooney viscosity (1 + 4, 150 °C)		24.4			77.5		47.4	
composition, wt %								
PE block		45			41		37	
ethylene		74.4			70.8		73.2	
ethylene in EP segment		53.5			50.5		57.5	
ENB		0.47			0.4		0.28	
stress/strain results								
temp, °C	20	20	20	20	20	60	20	60
comments	*a*		*b*		*b*			
100% modulus, MPa	3.9	4.9	4.8	3.6	3.7	2.3	4.1	2.9
tensile strength, MPa	5	16	15	21	17	3.7	28	10
elongation at break, %	1050	1065	950	900	750	440	700	450

[a] Uncoupled. [b] Reprocessed.

Table 9. Polymer Properties in a Roof Sheeting Application

	run 348A	run 348B	run 348C	run 348D	run 348E	EPDM[b]
cure properties[a]						
hardness, shore A						
20 °C	89	89	87	87	87	61
70 °C	85	85	79	79	77	54
94 °C	79	83	72	74	74	52
elongation, %	30	70	370	350	290	420
100% modulus, MPa			6	5.9	4.9	2.8
tensile strength, MPa	5.1	6.3	9.3	9.6	6.9	9.2
heat seal tensile strength MPa[c]	no seal	no seal	8.4	8.3	6.2	no seal

[a] 100 parts polymer 105 parts N650 black, 65 parts Sunpar 2280 oil. [b] 70/30 Vistalon 2727 and 3708 (Exxon Chemical Co.). [c] 2.54 cm overlap, seal at 148 °C for 15 min.

strength at 20 °C (17 MPa) but almost no strength at 60 °C (1 MPa).

Thus, we have shown that PE−EP−EPDM triblock polymers can be chain coupled to produce a reprocessible TPE with attractive properties. One potential application for these materials is in roof sheeting where the high ethylene content should provide excellent environmental stability. Also, as compared to vulcanized EPDM sheeting, joints between sheets can be formed by simple heat sealing rather than by expensive adhesive systems. Table 9 shows the properties of the series of polymers described in Table 7 in a typical roof sheeting formulation after curing with a sulfur−accelerator cure package. Also shown in the table are the results obtained with a commercial EPDM. Physical properties of the compounded 348 series of polymers exhibits the same trends as shown in Table 7 for the pure polymers coupled with sulfur dichloride. Polymers 348A and 348B formed a cross-linked network with low elongation at break that could not be heat sealed at a joint. On the other hand, polymers 348C and 348D gave tensile properties very similar to that of the commercial EPDM, and the strength of a heat sealed joint was almost the same as that of the bulk polymer. Sample 348E, in which the ENB was added very close to the end of the reactor had a lower tensile strength than samples 348C and 348D due to the reduced amount of EPDM block in the chain.

Conclusions

This work has demonstrated that PE−EP block polymers can be made with pseudo living Z−N catalysts when polymerization time for each block is well matched to chain growth time and catalyst decay rates. For high yields of multisegment block polymers, it is essential that the reaction time for each chain segment in the sequence provides sufficient time for segment growth, but minimizes the opportunity for chain transfer and catalyst decay. Ethylene polymerizes very rapidly with most Z−N catalysts. In this work, polymerization at 20 °C with an initial ethylene concentration of 0.05−0.1 mol/L gave PE with an M_n of 30 000 in 1.3 s reaction time. Thus to meet the residence time criteria for block polymer formation, the reactor system must be capable of adding monomer feeds at very short intervals. We have accomplished this using a tubular flow reactor with multiple side stream feeds. The difficulty of operating a semibatch reactor at these time scales explains why past attempts at making block polymers in high yields were largely unsuccessful.

Requirements for the catalyst system include very rapid chain initiation relative to propagation, minimal amounts of chain transfer, and, desirably, presence of a single active catalyst species to obtain narrow MWD and controlled CD products. The premixed $VCl_4/Al_2Cl_3Et_3$ catalyst has many of these characteristics in solution polymerization, but formation of the PE block gave unusual kinetics and unexpectedly broad MWD which may be related to polymer precipitation. More work would be required to better define the polymerization at these conditions and explain the differences in behavior during PE block and EP block polymerization. Despite uncertainties in the polymerization mechanism, we were able to get good correlations of the block polymerization data based on a simplified kinetic model. Because a tubular reactor with multiple side stream feeds can be operated at many different combinations of feed rate, feed composition, and feed placement, selecting the conditions to obtain a specified block structure in high yield can be challenging. The kinetic model was found to be a very valuable tool for this purpose, and in addition, it provides an estimate of some of the details of the polymer structure that are difficult to determine by direct measurement.

Yields of block polymer, either PE−EP or PE−EP−EPDM, exceeded 70% when side stream feed locations and total residence time were optimized. The composition and molecular weight of the EP and EPDM chain fragments are consistent with formation by chain transfer as described by the kinetic model. However, the PE chain fragments are difficult to separate from the PE block polymer and so were not characterized.

PE−EP diblocks have low strength, as expected, and are not suitable for most TPE applications. However, by making a PE−EP−EPDM triblock and chain coupling it via the olefinic unsaturation in the EPDM to produce nodular polymers with PE end blocks, we observe that tensile strength increases into the 12−18 MPa range. In this work, chain coupling was carried out with either SCl_2 or standard EPDM sulfur/accelerator cure packages. It is essential that the amount and composition of the EPDM block provides enough chain coupling to give the desired properties without forming an extensive cross-linked network. It appears that these objectives can be met with 5−15% EPDM block containing 1−2% ENB. Although, after coupling, a large fraction of the polymer may become insoluble in boiling toluene, the polymer can still be easily processed and will accept loadings of carbon black and oil.

Supporting Information Available: Two tables providing detailed reaction conditions. This material is available free of charge via the Internet at http://pubs.acs.org.

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