Table III
Effect of Formamide/Ethanol

entry	EtOH/HCONH$_2$[a]	MW[b]	yield, %
1	5/1	86 000	42
2	1/1	259 000	54
3	1/7	929 000	42

[a] Ratio of SM/Cat/S = 100/1/400. [b] Ratio of cis to trans isomers = 1/1.8.

Table IV
Homogeneous Polymerization of Deltacyclene

entry	ratio mol of SM/Cat/S	solvent (ratio)	MW[a]	yield, %
1	100/1/350	EtOH/PhH (1/3)	5 000	60
2	200/1/400	EtOH/THF (1/10)	35 000	68
3	100/1/400	H$_2$O/THF (1/10)	992 000	74

[a] Ratio of cis to trans isomers = 1/1–1.5.

M_w did increase with increasing amounts of formamide (Table III).

We also examined polymerization under conditions where the starting material and product would be completely soluble. Reaction in THF or benzene in the presence of hydroxylic solvents caused the solution to become highly viscous during the course of the reaction but remain as one phase. In general, these reaction conditions were inferior to those described above. However, when the polymerization was carried out in a mixture of water/THF, a high molecular weight polymer was isolated (Table IV, entry 3). No other changes were observed (i.e., olefin double-bond isomer ratio).

Measurement of the glass transition temperature, T_g, using differential scanning calorimetry (DSC) was attempted so as to more fully characterize the macromolecules. These experiments proved unsuccessful since no T_g was observed from −150 to +150 °C. Instead, a highly exothermic process was noted at ca. 135 °C. When the measurement was repeated on the same sample, a totally different curve was observed. When a sample of the polymer was heated in an inert atmosphere to 150 °C, the ratio of olefinic to aliphatic protons decreased. We have been unable to fully characterize this material to determine the nature of the reaction.

The chemistry described demonstrates the viability of preparing polymers from a ring-opening metathesis of deltacyclene. High molecular weight macromolecules have been isolated in excellent yield. The polymers synthesized have olefins that are rigidly held at defined distances due to the nortricyclane framework. Studies are in progress to exploit the unique features of these new molecules. The ROMP of substituted deltacyclenes is also under way, the results of which will be reported in due course.

Acknowledgment. This research was supported by the Natural Science and Engineering Research Council (NSERC) of Canada, the Bickell Foundation, the Ontario Centre for Materials Research (OCMR), and the University of Toronto. We thank Professors M. A. Winnik, J. E. Guillet, and W. F. Reynolds of the University of Toronto for helpful discussions and the DAAD (FRG) for the support of J.R. during his stay in Toronto. We also thank T. Huber of the University of Toronto for performing the ebuliometry measurements.

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(12) Gel permeation chromatography (GPC) was carried out on a Varian 5000 liquid chromatograph using an Ultrastyragel 10^4-Å or 500-Å column with THF as eluant.
(13) The M_w and M_n of the polymer were calculated from GPC analysis [vs poly(methyl methacrylate) standard]. To check the accuracy of this method, this value was compared to the M_n calculated from ebuliometry of a dilute solution of the polymer in refluxing benzene. The two values were within 15–20% of one another: Huber, T., unpublished results.
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Received May 8, 1989;
Revised Manuscript Received July 13, 1989

Supported Vanadium Catalyst for Isospecific Propylene Polymerization

Ziegler–Natta (ZN) catalysts for isospecific polymerization of α-olefins are mainly based on group IV transition elements. Vanadium compounds on the other hand have a propensity for syndioselectivity.[1] V(acac)$_3$/AlEt$_2$Cl[2a] and V(mbd)$_3$/AlEt$_2$Cl[2b] (mbd = 2-methyl-1,3-butanedianato) catalyze "living" syndiospecific polymerization of propylene

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at low temperatures. Vanadium ZN catalysts produce "random" ethylene-propylene copolymers whereas the copolymers obtained with titanium ZN catalyst tend to have "blocky" structures. Consequently, the main industrial usage of the former is for the manufacturing of ethylene-propylene elastomers.[3,4] In this paper we report that $MgCl_2$-supported vanadium catalysts[5] are highly isospecific for propylene polymerization; a full length paper will be published elsewhere.[6]

$MgCl_2$ (Toho Titanium) was purified, dehydrated, ball-milled with ethyl benzoate (EB), reacted with VCl_4 dissolved in *n*-heptane, and thoroughly washed.[7a] This CW–V catalyst was activated with $AlEt_3$ (TEA) and methyl-*p*-toluate (MPT) in a 3:1 ratio. Propylene was polymerized usually with $[V] = 2.6$ mM; $[TEA] = 42$ mM; $[C_3H_6] = 0.71$ M at 50 °C.

Monomer consumption begins immediately upon introduction of the coactivators. Polymerization reaches a maximum rate of 6×10^{-4} M s^{-1} within 10 min; it decays rapidly to a constant $R_p \sim 10^{-4}$ M s^{-1} after 20 min. The productivity is 30 kg of polymer (M V·h·M $C_2H_6)^{-1}$; up to 97% of the polymer is insoluble in refluxing *n*-heptane (isotacticity yield (IY) = 97%). Polymerizations were run with Al/V ratios from 10 to 334; highest productivity and IY were obtained at a ratio of 84.

The *n*-heptane-insoluble polymer is "100%" isotactic according to IR spectra[8] and ^{13}C NMR spectra, which contain only the *mmmm* peak, all other steric pentad having intensities less than the S/N ratio. The steric sequence distributions are consistent with stereochemical control by an enantiomorphic site model, implying primary migratory insertion of monomer. The *n*-heptane-soluble polymers have the diastereo sequence distribution typical for atactic microstructure: $[mmmm] = 0.20$; $[mmmr] = 0.11$; $[rmmr] = 0.04$; $[mmrr] = 0.15$; $[mmrm + rmrr] = 0.13$; $[mrmr] = 0.05$; $[rrrr] = 0.15$; $[rrrm] = 0.08$ and $[mrrm] = 0.07$. There are no NMR peaks or IR absorptions due to head-to-head and tail-to-tail inserted units.[6] Therefore, the polymerization is highly regiospecific.

The rate constant of propagation (k_p) and the kinetic isotope effect (KIE) were determined[7b] for the CW–V catalyst. The latter was obtained from the ratio of the specific radioactivities found in polypropylene by quenching a polymerization mixture with a stoichiometric amount of CH_3O^3H equivalent to all the reactive organometallic and metal–chlorine bonds (no KIE) and with an excess of titriated methanol (full KIE). The value of KIE was found to be 1.8 for the total propylene polymerization and 1.3 for the isotactic propylene polymerizations. A series of propylene polymerizations were then conducted and quenched with an excess of CH_3O^3H at 5-min intervals, the polymers were separated, and the specific activities in the total polymers and in the isotactic fractions were counted. Extrapolations to zero polymer yield gave the number of active vanadium–polymer bonds in the isotactic and the atactic fractions. Together with the rates of isospecific and nonspecific polymerizations, we found values of k_p to be 1580 and 58 M s^{-1}, respectively. From the slopes of the [metal–polymer bond] versus yield plot, the rate constants of chain transfer with TEA were found to be 2.0×10^{-3} and 3.0×10^{-3} s^{-1}, respectively, for the isospecific and nonspecific sites. The active sites are 0.02% and 0.06% of vanadium for $[C_i^*]$ and $[C_a^*]$, respectively.

There are striking similarities between the CW–V and CW–Ti systems. Both catalysts were found to have[7b] $k_{p,i} \gg k_{p,a}$. The isospecific and nonspecific active Ti sites have k_p values of 160 and 11 M s^{-1}, respectively.[9] The EPR of VCl_4 on $MgCl_2$ is characteristic for an axially symmetric $3d^1$ ion; the EPR parameters are very similar to VCl_4 supported on SiO_2.[10] The EPR signal intensity[7c] corresponds to 16.5% of the V^{4+} ions adsorbed on $MgCl_2$; it is 22.3% of the total upon reduction by TEA/MPT. Similarly, the CW–Ti catalyst contains 20–25% of EPR observable Ti^{3+} ions of the total Ti^{3+} determined by redox titration;[11] those Cl-bridged paramagnetic ions are dipolar broadened to beyond EPR detection. The ratio of EPR observable to silent paramagnetic V and Ti ions is comparable in the CW–V and CW–Ti catalysts. The rapid decay of R_p with polymerization time is similar in both systems, which had been attributed to deactivation of pairs of adjacent catalytic sites.[11,12]

The most notable difference between the two systems is the polymer MW. Polypropylenes obtained at 50 °C with the CW–Ti catalysts[13] have $\bar{M}_w = 2 \times 10^4 – 4 \times 10^5$; it is about 2×10^6 for the CW–V catalysts as determined by light scattering. GPC was not successful because of cutoff of the very high MW end. Therefore, neither $\bar{M}_n$ nor PD can be obtained. The three chain-limiting processes for the Ti system are β-hydride elimination, transfer to monomer, and transfer to TEA; the first dominates at low monomer pressure and [TEA] and the latter at high monomer pressure and high [TEA]. The higher polymer $\bar{M}_w$ found for the V system indicates less facile β-hydride elimination for a V–P species than a Ti–P species, where P is a polypropylene chain. Finally, both catalysts can produce polypropylenes having maximum IY of 97%; the deletion of MPT as the coactivator lowers IY to 80% for the CW–V system as compared to 70% for the CW–Ti catalyst activated with TEA alone.[14]

The changes in the polymerization behaviors of vanadium compound/$AlEt_2Cl$ catalysts upon supporting it on $MgCl_2$ are profound. The mechanism of propylene polymerization by the homogeneous vanadium catalyst is secondary (2-1) insertion and stereochemical control by the chirality of the last monomer unit.[15] This is changed, for the present CW–V catalyst, to primary (1-2) insertion and stereochemical control by the enantiomorphic catalytic site. In the case of the CW–Ti catalysts, $MgCl_2$ is said[16] to play the role of $TiCl_3$ by virtue of their similar crystal structures. The present results suggest that $MgCl_2$ imposes on the vanadium ions the same chiral and steric environment as existing in α, γ, and δ $TiCl_3$. In addition, $MgCl_2$ must also modify the electronic structure of the V–P species to greatly facilitate chain propagation by several thousand fold. In contrast to the CW–V catalytic activity given above, the activities for homogeneous $VCl_4/AlEt_2Cl$,[1] $V(acac)_3/AlEt_2Cl$,[2a] and $V(mbd)_3/AlEt_2Cl$[2b] systems are 0.01, 0.08 and 0.61 kg PP(M V·h·M $C_3H_6)^{-1}$, respectively. In the living propylene polymerization initiated by the third catalyst, the $\bar{M}_w$ of the polymer is only ca. 7000 (assuming linear increases of MW with time of polymerization).

There have been several important developments in ZN catalysts, all showing strong influence of the ligand environment for the transition-metal ion. These include racemic ansa-bridged group IV metallocene/MAO (=methylaluminoxane) catalysts for isospecific polymerizations of propylene and other α-olefins,[17,18] tetrabenzyltitanium/MAO catalysts for syndiospecific polymerization of styrene,[19] and isopropyl(cyclopentadienyl-1-fluorenyl)hafnium dichloride/MAO catalyst for syndiospecific polymerization of propylene.[20] The results of this paper reveal further means to control stereospecific molecular catalysts.

Acknowledgment is made to the donors of the Petroleum Research Foundation, administered by the American

Chemical Society, in support of this research.

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Received May 12, 1989;
Revised Manuscript Received August 29, 1989

Diffusion in Dilute Polystyrene/Poly(phenylmethylsiloxane) Blends

Two polymer blends in the homogeneous region have been investigated by dynamic light scattering so far. These are the polymer mixtures polystyrene (PS)/poly(phenylmethylsiloxane) (PPMS)[1,2] and poly(ethylene oxide) (PEO)/poly(propylene oxide) (PPO).[3,4] Both the mutual diffusion coefficient (or interdiffusion) D and the static structure factor $S(0)$ have been measured at different volume fractions Φ in the range 0.1–0.9 and discussed in the framework of recent theoretical models.[5–9] The pertinent conclusions emerged from these studies may be summarized as follows: (1) Thermodynamic interactions play a significant role in accordance with all theoretical treatments. Unfavorable segment–segment interactions lead to a reduced interdiffusion, i.e., $D < D°$, with $D°$ being a weighted average of the tracer diffusivities of the mixture components.[6–9] (2) If the glass transition temperature, T_g, of the blend varies with composition, then a major dependence on concentration is introduced in addition to those predicted by the theories.[2] (3) For unentangled Rouse chains, i.e., $D_i \sim M_i^{-1}$ (i = A and B, the blend components), the average mobility $D°$ is expected to be molecular weight (M) independent and verified experimentally.[4,11]

In a recent photon correlation study of very dilute homogeneous PS/PPMS blends ($\Phi_{PS} < 0.01$), the experimental D in the infinite dilution limit $\Phi_{PS} \rightarrow 0$ was reported to follow a molecular weight dependence close to $M^{-0.5}$ for M_w(PS) in the range 10 200–17 500 and constant M_w(PPMS) = 2600.[10] This trend was violated by the M_w(PS) = 2000 sample. In dilute polymer–polymer blends, T_g effects are unimportant and the knowledge of D is of considerable interest. There are, however, in our opinion several serious problems with the experimental conditions and analysis of those data. The used bulk PPMS sample was previously found to display significant dynamic light scattering arising from concentration fluctuations owing to the presence of oligomers.[12] This correlation function in the bulk PPMS will probably affect the experimental concentration correlation functions in the very dilute PS/PPMS blends as the associated scattering power is weak at low Φ_{PS}.[2] To extract the interdiffusion D, reported in ref 10, only a few initial points of normalized experimental correlation functions were used without regard to base line and amplitude. Moreover, in the analysis of D thus obtained, the importance of the static structure factor $S(0)$ (in the thermodynamic limit $q \rightarrow 0$, with q^{-1} being the probing wavelength) was entirely ignored although there was strong evidence of its influence (Figure 6 in ref 10). We have, therefore, undertaken the present investigation with the main objective to find the correct molecular weight dependence of $D°$ by improving the data quality and pursuing a correct analysis of the experimental D.

Experimental Section. One PPMS sample (M_w = 2600, $M_w/M_n \sim 1.6$) from Petrarch systems (Lot 45106) and PS samples (M_w = 1700, 3800, 9000, and 16 700) with polydispersity index $M_w/M_n \sim 1.04$ were used. Dilute PS/PPMS mixtures at constant 0.5 wt % PS concentration were carefully prepared using the procedure described elsewhere.[13] The dust-free mixtures yielded only inherent light-scattering intensity whose isotropic component arises from concentration and density fluctuations.

The experimental time correlation function of the scattered light intensity in the VV geometry was measured with a 28 log spaced delay channel Malvern (K7027) single-clipped correlator. The light source was an argon ion laser (Spectra Physics 2020) operating at a single mode at 488 nm with a stabilized power of 100 mW. Measurements and analysis of the homodyne correlation function $G(q,t)$ were all as previously described.[2,4]

Results and Discussion. The net concentration correlation functions $C(q,t) = [G(q,t)/A - 1]^{1/2}$ using a fixed base line A were found to have an almost exponential shape,[14] so that a meaningful average relaxation time τ can