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Characterization of the Stereostructure of Three Poly(1-butenes): Discrimination between Intramolecular and Intermolecular Distributions of Defects in Stereoregularity

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ABSTRACT: A very complete characterization of the stereostructure of three poly(1-butenes) was achieved by separating the polymers into components of increasing isotacticity with successive recrystallizations from hot *n*-heptane solutions and analyzing the components with ^{13}C nuclear magnetic resonance, gel permeation chromatography, and other techniques. The poly(1-butenes) analyzed were (1) a highly isotactic homopolymer prepared by using a conventional titanium chloride/alkylaluminum catalyst, (2) a moderately isotactic homopolymer prepared by using a variation of this conventional catalyst, and (3) a moderately isotactic homopolymer prepared by a high activity supported titanium chloride catalyst developed at Shell Development Co. It is shown that the two materials prepared by the conventional catalyst are predominantly mixtures of atactic molecules with highly isotactic molecules, while the material prepared by the high activity catalyst contains a large proportion of molecules of intermediate tacticity. The polymer of intermediate tacticity prepared by the conventional catalyst behaves like a plasticized thermoplastic, while the polymer of intermediate tacticity prepared by the supported catalyst shows more elastomeric properties.

Introduction

Polymerization of propylene, 1-butene, and higher α-olefins by Ziegler–Natta catalysts, which are combinations of a compound of a group IV–VIII (4–10)[22] transition metal with an organometallic compound of a group I–III (1, 2, 13) nontransition element, can produce polymers with a high degree of stereochemical regularity.[1] The most powerful experimental tool we have to determine the stereostructure of these polymers is ^{13}C nuclear magnetic resonance (NMR), which gives information about the stereochemical structure because the NMR chemical shifts of the carbon atoms are sensitive to the configuration of closely bonded neighbors.[2,3] Different measures characterizing the average degree of isotacticity of a polymer sample can be derived from the NMR spectrum of the whole polymer,[3] but to more completely determine the stereostructure of a polymer, it is useful to separate the polymer into components of varying isotacticity and then analyze each of these components. This gives information about the distribution of isotacticity among the polymer molecules, just as a separation on the basis of molecular weight gives information on the distribution of chain lengths among the polymer molecules.[4] Understanding the stereostructure of these polymers in detail is important in understanding the mechanism of olefin polymerization[5] and the relationship of these structures to the morphology and properties of the polymers.[6–10]

In this work three poly(1-butenes) were analyzed: (1) a highly isotactic homopolymer prepared by using a conventional titanium chloride/alkylaluminum catalyst, (2) a moderately isotactic homopolymer prepared by using a variation of this conventional catalyst, and (3) a moderately isotactic homopolymer prepared by a high activity supported titanium chloride catalyst developed at Shell Development Co. Each of these materials was separated into components varying in crystallizability by sequential crystallization from hot *n*-heptane solutions and isolation of the soluble and insoluble components. More specifically, an initial recrystallization of the whole material was followed by subsequent recrystallization of the soluble component, the insoluble component, or both, and this procedure was repeated until the desired degree of separation was obtained, the ratio of heptane to polymer being adjusted at each step of the separation. The resulting components were then analyzed by ^{13}C NMR, gel permeation chromatography (GPC), and other techniques. From this work a very complete characterization of the stereostructure of these materials was achieved, and it was found that the two materials prepared by the conventional catalysts were predominantly mixtures of atactic molecules with highly isotactic molecules, while the material prepared by the high activity catalyst contains a large proportion of molecules of intermediate tacticity. The physical properties of these materials reflect these structural differences.

Materials and Methods

Sample I is a commercial highly isotactic poly(1-butene) homopolymer manufactured by Shell Chemical Co. and made with a conventional titanium chloride/alkylaluminum catalyst. Sample II is a poly(1-butene) homopolymer of intermediate isotacticity made with the same conventional catalyst but without a selectivity control agent. Sample III is a poly(1-butene) homopolymer of

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intermediate tacticity made by using a high activity supported titanium chloride catalyst. The characterization of these materials is given in this paper.

Crystallizability Separation. The materials were separated by recrystallization from boiling *n*-heptane solutions, a procedure that should separate material predominantly by crystallizability, and therefore by isotacticity.[4,11] The original polymer, or a component obtained from a previous separation, was dissolved in boiling *n*-heptane in a flask with an attached reflux condenser and the flask was heated by steam. After the polymer was completely dissolved, the solution was cooled undisturbed to room temperature overnight, and the resultant gel was washed with room temperature heptane. The insoluble component was separated by vacuum filtration and dried in a vacuum oven at 70 °C. The heptane was then evaporated from the soluble component by using a Wheaton Heidolph Type W1 rotary evaporator, and that component was then collected. The weight of each component was recorded. For successive separations, different ratios of heptane volume to starting material weight were used, as is indicated in Figure 1.

^{13}C Nuclear Magnetic Resonance. Samples for analysis were prepared by dissolving 100–500 mg (usually at least 300 mg) of polymer in 2 mL of 1,2,4-trichlorobenzene in a 10-mm-diameter NMR tube. The tube containing the sample and solvent was placed in an aluminum heating block and heated to about 140 °C, with a stream of dry nitrogen gas passed through the solution both to agitate it and hasten dissolution and to minimize degradation of the polymer. Finally, a 2.5-mm-diameter capillary tube containing ^{13}C-depleted DMSO-d_6 for a deuterium lock was inserted and held concentrically by two Teflon plugs.

Spectra were obtained at 90.55 MHz with a Bruker WH-360 NMR spectrometer with quadrature detection, proton broad-band decoupling, temperature 408 K, spin rate 35–50 Hz, pulse width 15 μs (90° tip), relaxation decay 20 s, spectral width 14285 Hz, and filter width 12000 Hz. The spectra were analyzed by an ASPECT 2000 computer using a transform size of 32K points. The rf carrier was set (01 = 11 000 Hz) such that the spectral lines due to the solvent would be "folded back" and thus have reduced intensity after Fourier transformation of the free induction decay (FID). Polymers with little stereoregularity required a few hundred scans (taking 1–2 h) to obtain a satisfactory signal-to-noise ratio, while highly isotactic polymers required several thousand scans. The FID's were processed by using either the sinebell procedure[12,13] or, mostly for polymers with little stereoregularity, the Lorentz–Gaussian transformation.[14]

A typical spectrum is shown in Figure 2, which also shows the peak assignments for the eight pentads or pentad combinations (*mmmm*), (*mmmr*), [(*mmrr*) + (*rmmr*)], [(*mmrm*) + (*rmrr*)], (*mrmr*), (*rrrr*), (*mrrr*), and (*mrrm*). The procedure for analyzing the spectrum was developed at Shell Development Co.;[15] a published description of the NMR analysis of poly(1-butene) is given in ref 16. A correction was made for overlap of satellite peaks from the *mmmm* peak by setting (*mmmm*) = (*mmmm*)′ + 0.01(*mmmm*)′ and (*mmmr*) = (*mmmr*)′ − 0.01(*mmmm*)′, where (*mmmm*)′ and (*mmmr*)′ are the uncorrected pentad intensities. From the measured pentad intensities, the relative intensities of triads and monads were then calculated by using well-known relationships.[3] From these the like-configuration sequence length $\langle l \rangle = 1/(r)$ and other average sequence lengths[6] were calculated. These are described and tabulated in Table V.

Gel Permeation Chromatography. Molecular weight distributions of the original materials and each component were obtained by using a high-temperature gel permeation chromatograph designed and built at Shell Development Co. A sample was placed in a stainless steel container along with 50 mL of *o*-dichlorobenzene containing 0.05% decane. The samples were purged with helium for 15 min; then the container was pressurized with helium to about 180 psi to facilitate later injection of the sample. The container was then placed on a rotator mounted on the back of an oven, and the sample was heated to 150 °C and rotated at 6 rpm for 1.5 h to dissolve the polymer. After dissolution, the samples were injected through a stainless steel injection port heated to 175 °C into a column set of Du Pont SE-4000, SE-1000S, and SE-60S columns connected in series and heated to 150 °C. The columns were initially calibrated with five polypropylene narrow molecular weight distribution standards and three alkyl hydrocarbons, and subsequently each new column set was recalibrated with a secondary broad molecular weight distribution poly(1-butene) standard. The output from the column was detected by a Wilks Miran IA infrared detector set at 135 °C.

Differential Scanning Calorimetry. The original materials and each component were analyzed by using a Perkins-Elmer DSC-2 differential scanning calorimeter. Each sample was aged at least 10 days to assure that the crystalline phase would be in the stable form-II crystal structure[9] and then was heated at a rate of 10 °C/min to 150 °C to obtain a melting curve, cooled at 10 °C/min to obtain a cooling curve, heated to 60 °C and maintained there for 5 min to complete any crystallization (60 °C is about the temperature the crystallization rate reaches a maximum[17]), and then heated again at 10 °C/min to 150 °C to obtain a second heating curve. The melting temperature T_m for both heating curves and the crystallization temperature T_c for the cooling curve can be defined as the temperatures at which the rates of heat absorption or evolution reach a maximum. The poly(1-butene) was assumed to be in form I for the first heating,[9] and the fraction crystalline ϕ was obtained by dividing the heat evolved by 30 cal/g.[18] For the cooling and second heating, the poly(1-butene) was assumed to transform to and from form II, and the fraction crystallization was obtained by dividing the heat absorbed or evolved by 17 cal/g.[18]

X-ray Diffraction. The crystallinity of one of the components was measured by using a wide-angle X-ray diffraction measurement. The spectrum was obtained by using a Phillips PW-1316/90 X-ray diffractometer operating at 40 kV and 20 mA, using Cu Kα radiation and equipped with a graphite crystallization monochromator preceding a scintillation detector. The peak at Bragg angle $2\theta = 11.8°$ was assigned to the form-II crystal and the peak at $2\theta = 10°$ was assigned to the form-I crystal. The crystallinity was determined by the procedure given in ref 19.

Stress–Strain Measurements. Thin films were compression molded from the sample being investigated. The films were mounted in an Instron with an initial jaw separation of 1 in., the samples having an even width of $^3/_{32}$ in. between the jaws. The cross-head speed was 10 in./min. 3–5 measurements were taken for each sample, and the measurements were averaged.

Results and Discussion

The separation scheme and results for the three materials are shown in Figure 1. The results of ^{13}C NMR analysis of the original materials and each component are given in Table I. Molecular weight averages from gel

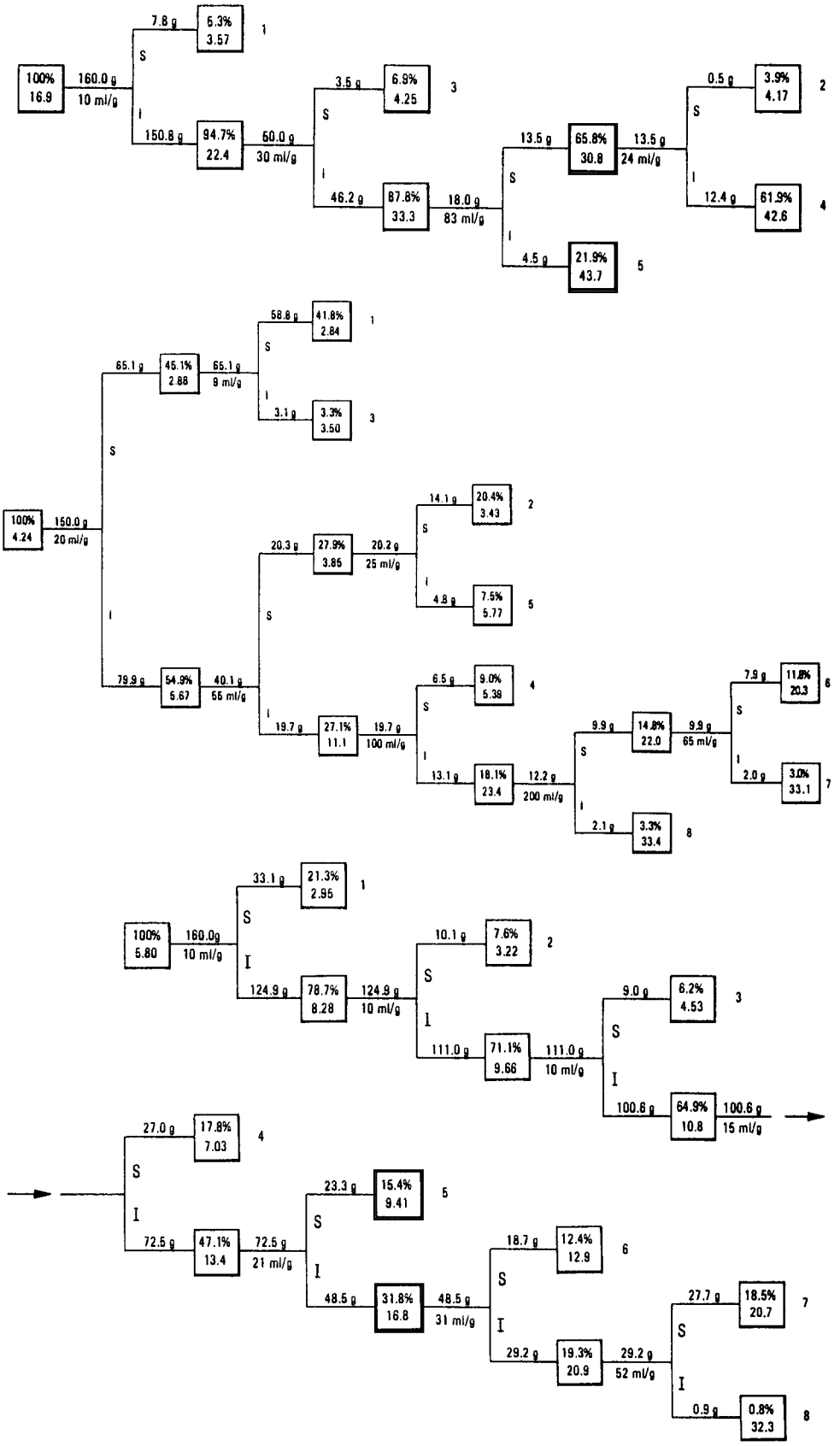

Figure 1. Separation procedures: The percentage given in each box is the weight of the component as a percentage of the weight of the original material. The second number given in each box is the average like-configuration sequence length of the component. The sequence lengths of the original material and each of the final components were determined from the NMR spectrum of the sample, while the sequence lengths of the intermediate components were calculated from the sequence lengths and the like-configuration sequence length number fractions of the final components. The line to the right of the box for all but the final components gives the weight of material used for that step of the separation, while the number below the same line gives the volume of heptane per weight of polymer used for that step. S denotes the soluble component, while I denotes the insoluble component. The figure above the line to the left of boxes for all but the original sample gives the weight of material collected for that component. In calculating the weight percentages of each of the components, it has been assumed that half of the material lost in the step belongs with the soluble component and the other half belongs with the insoluble component, so at each step of the separation the weight percentages total 100%. (top) sample I; (middle) sample II; (bottom) sample III.

Table I
NMR Spectra

i	(mmmm)	(mmmr)	(mmrr) + (rmmr)	(mmrm) + (rmrr)	(mrmr)	(rrrr)	(mrrr)	(mrrm)
				Sample I				
original	0.875	0.029	0.034	0.020	0.012	0.010	0.007	0.013
1	0.475	0.104	0.128	0.092	0.045	0.046	0.043	0.066
2	0.542	0.090	0.117	0.081	0.039	0.042	0.036	0.053
3	0.564	0.091	0.104	0.071	0.039	0.034	0.034	0.064
4	0.946	0.011	0.019	0.010	0.004	0.004	0.002	0.004
5	0.947	0.011	0.018	0.011	0.004	0.004	0.002	0.004
				Sample II				
original	0.566	0.077	0.104	0.081	0.039	0.042	0.041	0.050
1	0.354	0.011	0.151	0.127	0.061	0.066	0.054	0.078
2	0.470	0.093	0.126	0.099	0.048	0.050	0.046	0.069
3	0.461	0.102	0.133	0.099	0.049	0.050	0.043	0.063
4	0.653	0.066	0.084	0.063	0.031	0.031	0.026	0.046
5	0.676	0.058	0.081	0.059	0.028	0.030	0.029	0.037
6	0.906	0.017	0.023	0.017	0.010	0.011	0.005	0.011
7	0.938	0.013	0.015	0.011	0.007	0.006	0.003	0.006
8	0.929	0.016	0.024	0.008	0.011	0.003	0.003	0.005
				Sample III				
original	0.705	0.054	0.070	0.042	0.021	0.042	0.027	0.040
1	0.430	0.094	0.127	0.090	0.042	0.093	0.061	0.064
2	0.475	0.090	0.117	0.082	0.037	0.083	0.055	0.060
3	0.613	0.072	0.091	0.057	0.027	0.055	0.040	0.042
4	0.754	0.051	0.059	0.030	0.017	0.030	0.021	0.038
5	0.807	0.039	0.051	0.024	0.016	0.021	0.016	0.027
6	0.860	0.027	0.038	0.017	0.012	0.016	0.011	0.020
7	0.907	0.017	0.025	0.014	0.012	0.009	0.006	0.011
8	0.925	0.032	0.013	0.008	0.006	0.005	0.004	0.006

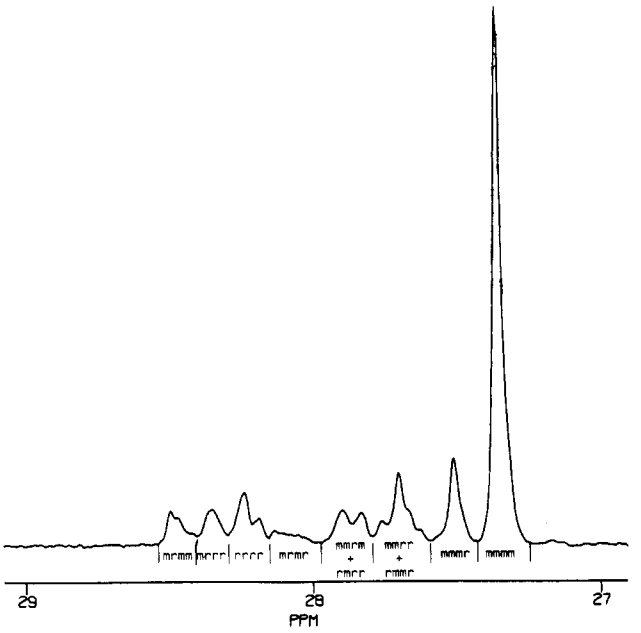

Figure 2. ^{13}C NMR spectrum of sample III component 2.

Table II
Molecular Weight Averages

i	$10^{-3}\bar{M}_n$	$10^{-3}\bar{M}_w$	$10^{-3}\bar{M}_z$	$Q = \bar{M}_w/\bar{M}_n$
		Sample I		
original	68	818	2917	12.1
1	11	151	1312	13.8
3	18	246	1563	13.4
2 + 4 + 5	113	849	2960	7.49
		Sample II		
original	58	943	3552	16.2
1	32	735	3088	23.1
2	34	938	3798	27.9
3	38	795	3388	21.0
4	43	1019	3601	23.5
5	42	969	3302	23.2
6	101	713	2204	7.05
7	119	720	2197	6.05
8	119	1117	3996	9.39
		Sample III		
original	90	591	2555	6.59
1	32	215	830	6.72
2	48	339	1501	7.07
3	79	441	1669	5.60
4	119	506	1632	4.26
5	111	393	1027	3.55
6	111	458	1424	4.11
7	127	584	1889	4.62
8	123	802	3256	6.52

permeation chromatography are given in Table II. Parameters from differential scanning calorimetry are tabulated in Table III. The results of the measurement of stress–strain curves are shown in Figure 3, and parameters for these measurements are tabulated in Table IV.

The purpose of the separation was to separate the polymer molecules on the basis of crystallizability, which in turn should be based on isotacticity. One would expect that a separation into liquid and crystalline phases should, except for very low molecular weights, depend primarily on the crystallizability and not on molecular weight.[4,11] There is some separation by molecular weight in these experiments, however, with the more isotactic components having higher average molecular weights. Whether this is a result of some separation by molecular weight in the separation steps or whether it is incidental in that the higher molecular weight chains are more isotactic is difficult to assess.

From the relative intensities of the pentad peaks in the NMR spectra tabulated in Table I, various average block lengths can be calculated, as tabulated in Table V. A more detailed description of these averages is given in ref 3. Also tabulated in Table V is the weight fraction and the number fraction of like-configuration sequences for each component; the number fraction of like-configuration sequences is defined and calculated as described in the Appendix. Since the various average sequence lengths are number averages,[3] the number fraction of like-configuration se-

Table III
DSC Measurements[a]

	first heating		cooling		second heating	
i	T_m, °C	ϕ	T_c, °C	ϕ	T_m, °C	ϕ
			Sample I			
original	121	0.46	58	0.43	115	0.46
1	*g*		*b*		*h*	
2	*i*		*b*		*j*	
3	*k*		*b*		*b*	
4	*l*		78	0.53	116	0.50
5	133[m]	0.68	81	0.53	117	0.52
			Sample II			
original	110	0.23	*b*		106	0.14
1	*n*		*b*		*b*	
2	99[o]	0.17	*b*		*b*	
3	*p*		*b*		*b*	
4	110	0.31	49	0.19	104	0.20
5	110	0.27	59	0.21	104	0.22
6	117	0.46	76	0.46	112	0.49
7	124[q]	0.50	81	0.49	114	0.50
8	*r*		81	0.52	116	0.52
			Sample III			
original	111	0.34	59	0.23	107	0.27
1	*a*		*b*		*c*	
2	*d*		*b*		*e*	
3	100	0.26	*b*		100	0.12
4	109	0.38	38	0.28	105	0.25
5	110	0.42	44	0.32	106	0.31
6	111	0.44	57	0.38	107	0.35
7	115	0.48	70	0.45	109	0.43
8	*f*		79	0.41	113	0.45

[a] Small peaks at 48, 65, and 78 °C. [b] No discernible peak. [c] Small peaks at 74 and 82 °C. [d] Peaks at 48 and 90 °C. [e] Peak at 76 °C. [f] Peaks at 87, 99, and 115 °C. [g] Small peaks at 46, 65, and 83 °C. [h] Small peaks at 68 and 82 °C. [i] Peaks at 44, 53, and 86 °C. [j] Peak at 82 °C. [k] Peaks at 46 and 96 °C. [l] Peaks at 105, 118, and 134 °C. [m] Additional small peaks at 101 and 117 °C, crystallinity calculated by using area of all three peaks. [n] Small peak at 46 °C. [o] Additional small peak at 46 °C. [p] Small peaks at 46 and 82 °C. [q] Left shoulder on peak at 119 °C. [r] Peaks at 87, 95, 101, 117, and 131 °C. [s] T_m is the melting temperature, T_c is the crystallization temperature, and ϕ is the fraction crystalline.

quences is useful in calculating the average sequence lengths of the intermediate components from those of the final components. The average like-configuration sequence length of each of the components is included in Figure 1, along with the calculated average like-configuration sequence lengths of intermediate steps in the separations. The final components have been numbered in order of increasing like-configuration sequence length.

From the results summarized in Figure 1, it appears that the molecules of sample III have an even distribution of isotacticities, with the bulk of the material being of intermediate tacticity, while samples I and II are essentially blends of relatively atactic material and highly isotactic material, the differences between the two samples being the relative proportion of the two components. In samples I and II components of only either quite low or quite high isotacticity could be separated, while in sample III components of intermediate tacticity were readily separated. This interpretation is supported by considering the volume of heptane relative to the weight of the polymer used in each step of the separation. Two examples can be considered to illustrate how the data support this interpretation.

As a first example, we can compare the separations of samples II and III. In separating sample III, it was found that gradually increasing the relative amount of heptane to polymer allowed the separation of material of increasingly greater isotacticity. In contrast, after the first step

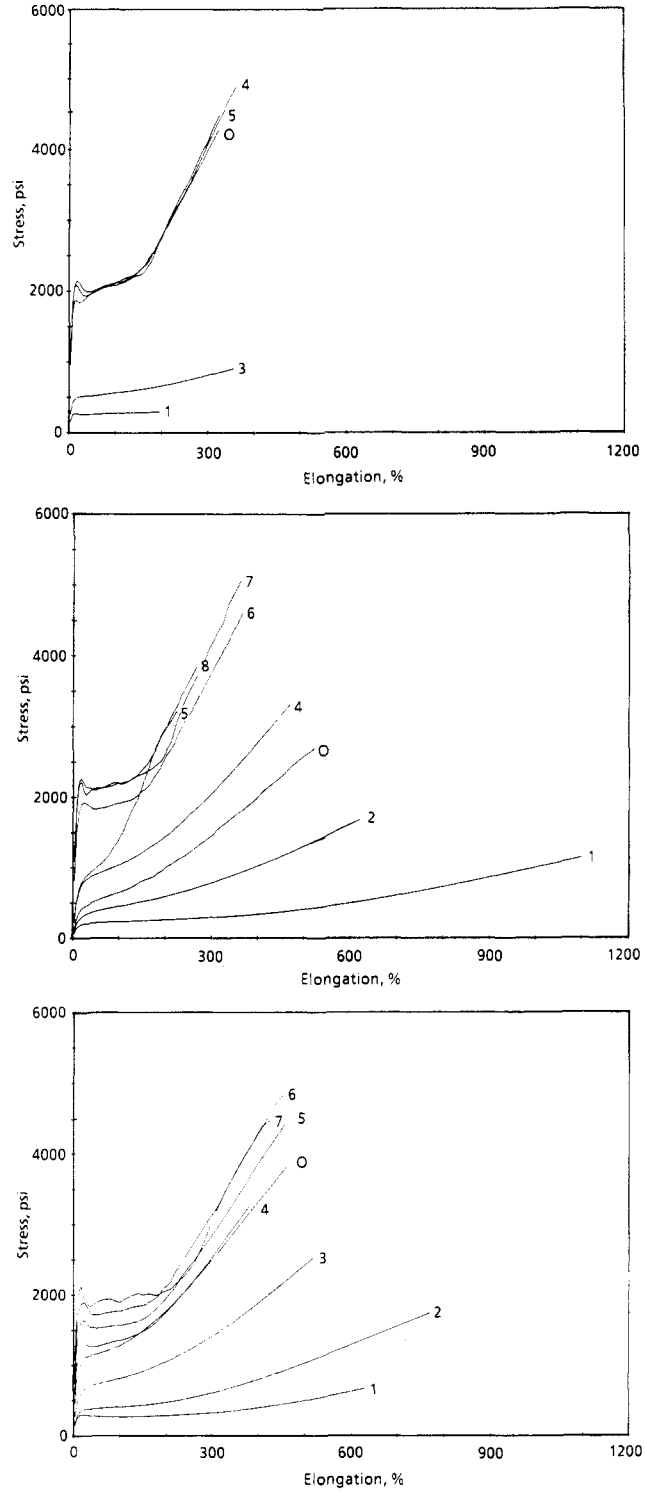

Figure 3. Averaged stress–strain curves for original material (0) and components: (top) sample I; (middle) sample II; (bottom) sample III.

of the separation of sample II, in which the material separated about equally into a component of low isotacticity and another of somewhat higher isotacticity, further separation of the soluble component yielded only a very small quantity of material with just slightly higher isotacticity, and further separation of the insoluble component yielded only additional material of low isotacticity along with material of relatively high isotacticity.

As a second example, we can compare the separations of samples I and III. In the separation of sample I, only a small amount of material of low isotacticity was obtained, the remainder of the material being highly isotactic. In

Table IV
Tensile Measurements

i	Young's modulus, psi	stress at break, psi	elongation at break, %
	Sample I		
original	30 300	4570	375
1	5 090	350	370
3	8 460	1140	490
4	30 200	5180	391
5	36 025	4854	358
	Sample II		
original	5 330	2860	658
1	2 310	1350	1276
2	3 510	2080	746
4	9 490	3730	531
5	8 930	3030	466
6	25 300	5080	411
7	36 900	5340	389
8	37 800	4410	319
	Sample III		
original	13 900	4220	537
1	4 800	783	722
2	5 200	1950	863
3	8 350	2690	556
4	17 500	4010	477
5	22 300	4710	505
6	25 000	5020	477
7	31 900	4830	459

the third step of the sample I separation, the use of 83 mL of heptane per gram of polymer still resulted in a substantial amount of insoluble material, while in the last step of the sample III separation, the use of 52 mL of heptane per gram of polymer almost completely dissolved the material. While differences in molecular weight may account for some of this difference, it seems likely that there is little material in sample III that is as highly isotactic as a substantial portion of sample I. Indeed, even though the most highly isotactic components of sample II are not as highly isotactic as the most highly isotactic components of sample I, they still appear to be more highly isotactic than all but a very small portion of sample III.

While a qualitative analysis of the data supports these conclusions, a quantitative analysis is helpful to both express this more clearly and make explicit the assumptions underlying the analysis. A procedure for determining the distribution of molecules of varying isotacticities from crystallizability separation data is described in the Appendix. The procedure uses the like-configuration sequence length as a measure of the isotacticity of a polymer molecule and assumes both that one-half of the like-configuration sequences of a component are below the average sequence length and one-half above and that the overlap of the distributions of sequence lengths between components is small (in other words, that the mean and median of the distribution of the like-configuration sequence lengths of the molecules in the component are the same and that the distribution is relatively monodisperse). Of course, these assumptions are not necessarily valid, but in the absence of more detailed information on the process of recrystallization they lead to a reasonable first approximation to the distribution of isotacticity within the sample.

In Figures 4 and 5 the cumulative weight distributions and weight densities of molecules with given like-configuration sequence lengths for the three materials are shown. These were calculated from the data in Table V by using the procedure outlined in the Appendix. The cumulative distributions are plotted as a straight-line fit between the calculated points, while the densities are the derivatives

Table V
Average Isotactic Sequence Lengths[a]

i	$w^{(i)}$	$n^{(i)}$	$\langle l \rangle$	f_m	$\langle l_m \rangle$	f_r	$\langle l_r \rangle$
			Sample I				
original			16.9[b]	0.941	31.7	0.059	1.99
1	0.053	0.247	3.57	0.720	5.80	0.280	2.26
2	0.039	0.156	4.17	0.760	7.03	0.240	2.22
3	0.069	0.271	4.25	0.762	7.40	0.235	2.27
4	0.619	0.242	42.6	0.977	75.7	0.024	1.82
5	0.219	0.084	43.7	0.977	75.3	0.023	1.76
			Sample II				
original			4.24[c]	0.764	7.40	0.236	2.28
1	0.418	0.581	2.84	0.647	4.16	0.353	2.27
2	0.204	0.235	3.43	0.709	5.58	0.291	2.29
3	0.033	0.037	3.50	0.715	5.55	0.285	2.22
4	0.090	0.066	5.39	0.814	9.82	0.186	2.24
5	0.075	0.051	5.77	0.827	10.8	0.173	2.26
6	0.118	0.023	20.3	0.951	42.3	0.049	2.19
7	0.030	0.004	33.1	0.970	64.0	0.030	1.99
8	0.033	0.004	33.4	0.970	53.2	0.030	1.64
			Sample III				
original			5.80[d]	0.827	13.0	0.173	2.71
1	0.213	0.425	2.95	0.661	5.43	0.339	2.79
2	0.076	0.139	3.22	0.690	6.19	0.310	2.79
3	0.062	0.081	4.53	0.779	9.41	0.221	2.67
4	0.178	0.149	7.03	0.858	16.1	0.142	2.68
5	0.154	0.096	9.41	0.894	20.7	0.106	2.46
6	0.124	0.057	12.9	0.922	29.3	0.078	2.47
7	0.185	0.053	20.7	0.952	41.9	0.048	2.13
8	0.008	0.001	32.3	0.969	63.4	0.031	2.02

[a] i is the component number, $w^{(i)}$ is the weight fraction of component i, $n^{(i)}$ is the number of like-configuration sequences in the ith component as a fraction of the number of like-configuration sequences in the original sample, $\langle l \rangle = 1/(r)$ is the like-configuration sequence length, $f_m = (mm) + (1/2)(mr)$ is the fraction of linkages involved in meso additions, $\langle l_m \rangle = [(mm) + (1/2)(mr)]/[(1/2)(mr)]$ is the average sequence length of meso additions, $f_r = (rr) + (1/2)(mr)$ is the fraction of linkages involved in racemic additions, and $\langle l_r \rangle = [(rr) + (1/2)(mr)]/[(1/2)(mr)]$ is the average sequence length of racemic additions. [b] $\langle l \rangle$ for original calculated from component measurements = 16.6. [c] $\langle l \rangle$ for original calculated from component measurements = 3.95. [d] $\langle l \rangle$ for original calculated from component measurements = 5.88.

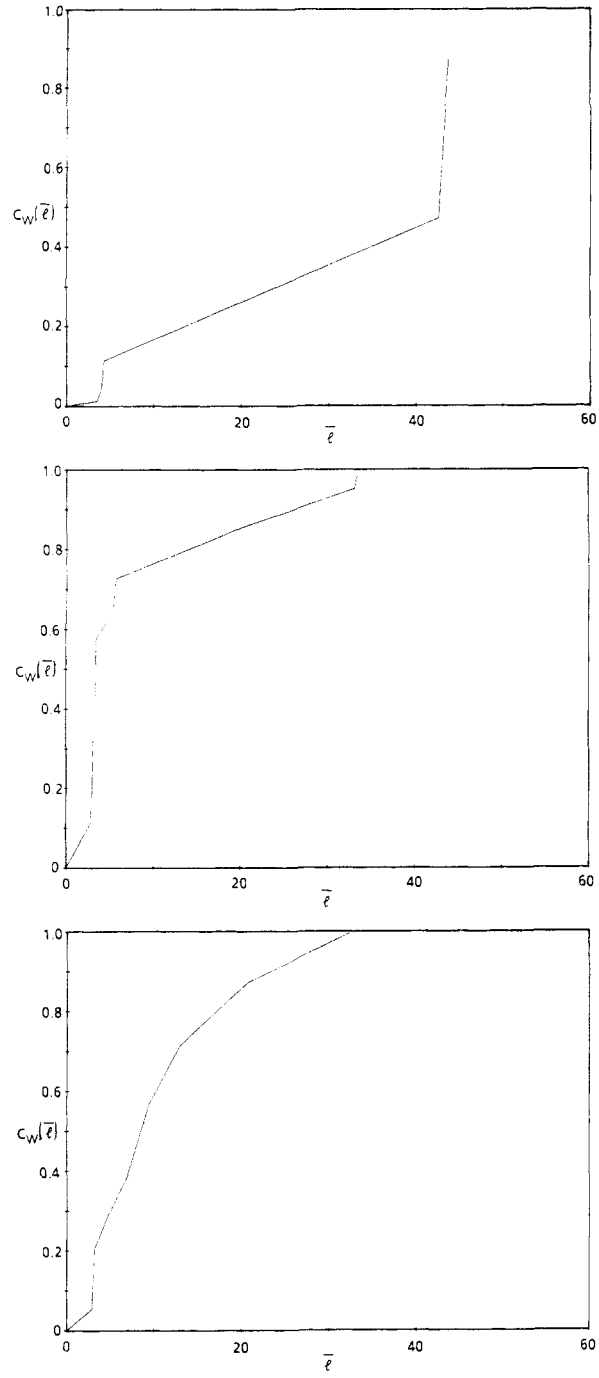

Figure 4. Cumulative weight distribution of molecules of given average like-configuration sequence length: (top) sample I; (middle) sample II; (bottom) sample III.

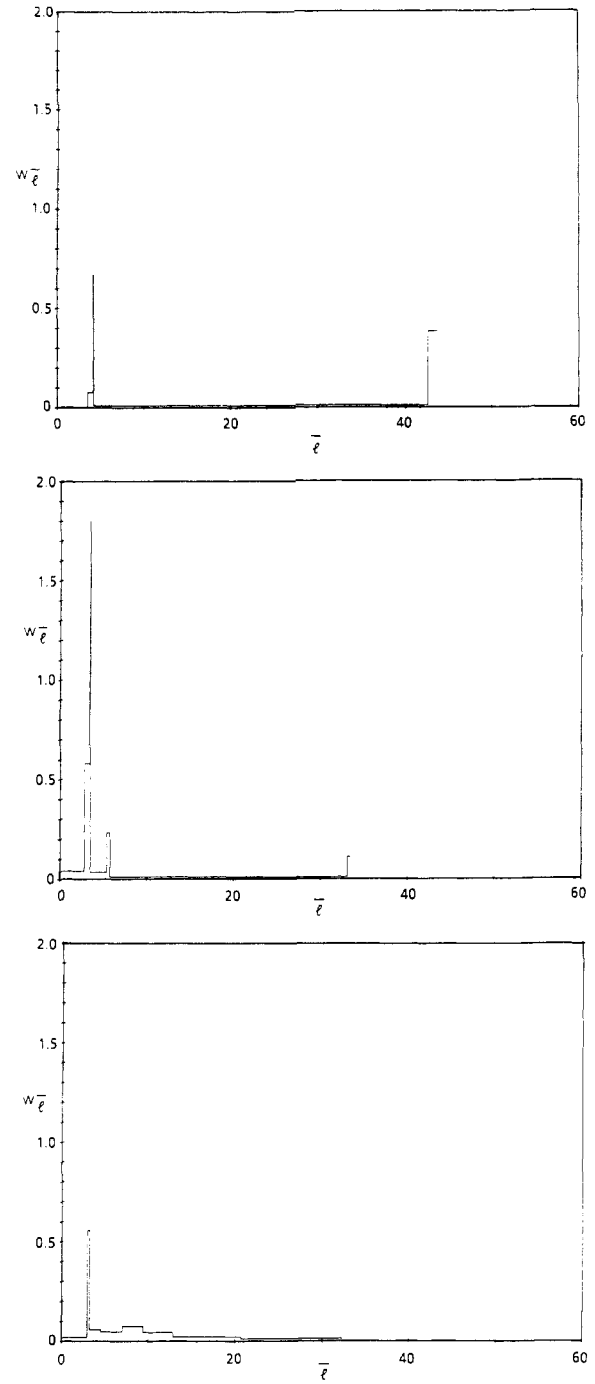

Figure 5. Weight density of molecules of given average like-configuration sequence length: (top) sample I; (middle) sample II; (bottom) sample III.

of the plotted distributions. These calculated cumulative distributions terminate before reaching unity because there is not enough data to determine the distribution beyond the last point plotted. Therefore, the calculated weight densities terminate at a lower isotacticity than they should because there are not enough data to determine the density beyond the last point plotted. Since numerical differentiation of inexact data is inherently unstable in that small errors in the integral curve can result in large errors in the derivative curve,[20] the densities are prone to errors, and some of the sharpness and fluctuation of the peaks in the densities reflect the relatively small number of data points obtained and random experimental error.

The results of this analysis, as shown in Figures 4 and 5, are consistent with the interpretation of the data given previously. Sample III contains a relatively broad distribution in the isotacticity of the material, with much of the material of intermediate isotacticity. In contrast, samples I and II are mixtures of molecules of low and high isotacticity, the two samples differing in the relative quantity of each of these two materials.

As shown in Table II, the components of higher isotacticity also consist of material with higher molecular weights. In samples I and II, the most highly isotactic components also have noticably narrower molecular weight distributions as well as noticably higher molecular weights compared to the components of low isotacticity. In sample III all of the components have quite narrow molecular weight distributions, and there is a fairly regular increase in molecular weight with increasing isotacticity.

Differential scanning calorimetry measurements show that the more atactic components often exhibit abnormal

heating curves and no discernible crystallization upon cooling. In general, there is an increase in the melting and crystallization temperatures and an increase in the crystallinity with increasing isotacticity, as one would expect. From an X-ray diffraction scan of the component 1 material from the sample II separation, a crystallinity of 17% was calculated, so the lack of clearly discernible crystallinity from the differential scanning calorimetry measurements should not be interpreted as a total lack of crystallinity. Between the different samples, sample I has a higher fraction crystalline than samples II and III, and sample III in turn has a higher fraction crystalline than sample II.

Stress–strain measurements show that among the components of a particular material, there is with increasing isotacticity a more pronounced necking, an increase in the stress at yield and stress at break, and a decrease in the elongation at break. Between the different samples, sample I show typical properties of a thermoplastic, sample II shows the weakening typical of plasticization of thermoplastics, and sample III shows more elastomeric properties.

This work indicates that the defects in stereoregularity are concentrated in specific molecules for the polymers prepared by the conventional catalyst and are distributed more evenly between molecules for the polymer prepared by the supported catalyst. The polymer of moderate isotacticity prepared by the conventional catalyst would be expected to behave like a plasticized thermoplastic, while the polymer of moderate isotacticity prepared by the supported catalysts would be expected to have a more extensive crystalline network and to be more elastomeric, as is confirmed by the measurement of physical properties.

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Appendix

A Procedure for Determining the Distribution of Molecules with Given Like-Configuration Sequence Lengths from Isotacticity Separation Data for Linear 1,2-Stereoregular Polymers. Initially, we will think of our material as an infinitely long polymer with like-configuration sequences of varying lengths. A like-configuration sequence consists of a run of monomer units joined by meso additions and terminated on both ends by racemic additions, the length of the sequence being the number of monomer units in the sequence.[3] If $\hat{N}_l$ is the number of sequences containing l monomer units, then the number fraction of sequences containing l monomer units is given by

$$\hat{n}_l = \hat{N}_l/N$$

where

$$N = \sum_j \hat{N}_j$$

is the total number of sequences in the sample. We define the number-average sequence length of the sample as

$$\langle l \rangle = \sum_l l\hat{n}_l = M/N$$

where

$$M = \sum_l l\hat{N}_l$$

is the total number of monomers in the sample. This is consistent with the definition of like-configuration sequence length given in ref 3.

We now take into consideration the heterogeneity in isotacticity among molecules by considering the material to be an assembly of molecules of varying lengths, each molecule in turn consisting of isotactic sequences of varying lengths. We can describe a given molecule by specifying the number of monomer units in the molecule k and the mean sequence length for the molecule

$$\bar{l} = \sum_l lN^*_l / \sum_l N^*_l = k/N^*$$

where N^*_l is the number of sequences of length l in the molecule and

$$N^* = \sum_l N^*_l$$

is the total number of sequences in the molecule. If $N_{k,\bar{l}}$ is the number of molecules of length k with mean sequence length $\bar{l}$, then the number fraction of molecules with k monomer units and a mean sequence length $\bar{l}$ is given by

$$n_{k,\bar{l}} = N_{k,\bar{l}} / \sum_{i,j} N_{i,j}$$

where

$$\sum_{i,j} N_{i,j}$$

is the total number of molecules in the sample. For a real sample with finite chain lengths, the possible values of $\bar{l}$ will be a finite set of rational numbers, so the summations over indices specifying $\bar{l}$ are over all possible values of $\bar{l}$ subject to any given constraints, not just over integral values.

We now define

$$N_{\bar{l}} = (1/\bar{l}) \sum_k kN_{k,\bar{l}}$$

as the number of like-configuration sequences in molecules with a mean sequence length $\bar{l}$. The corresponding number fraction is given by

$$n_{\bar{l}} = N_{\bar{l}}/N$$

where

$$N = \sum_{\bar{l}} N_{\bar{l}} = \sum_{k,\bar{l}} (k/\bar{l}) N_{k,\bar{l}}$$

is, as defined previously, the total number of sequences in the sample. The number-average sequence length of the sample is then

$$\langle l \rangle = \sum_{\bar{l}} \bar{l} n_{\bar{l}}$$

which is equivalent to our earlier definition; since

$$\sum_{\bar{l}} \bar{l} N_{\bar{l}} = \sum_{k,\bar{l}} kN_{k,\bar{l}}$$

is the total number of monomer units in the sample,

$$\langle l \rangle = M/N$$

as before.

The number density of sequences in molecules with a mean sequence length l is given by specifying $n_{\bar{l}}$ for all $\bar{l}$, and the cumulative, or integral, number distribution is given by

$$C_n(\bar{l}) = \sum_{j \le \bar{l}} n_j$$

The corresponding weight fraction is given by

$$w_{\bar{l}} = \bar{l} n_{\bar{l}} / \sum_j j n_j$$

The weight density of material in molecules with a mean sequence length $\bar{l}$ is given by specifying $w_{\bar{l}}$, and the cumulative, or integral, weight distribution is given by

$$C_w(\bar{l}) = \sum_{j \le \bar{l}} w_j$$

We assume that the original sample is separated into m components, with the weight of the ith component as a fraction of the weight of the original sample given by $w^{(i)}$ and the average sequence length of the ith component given by $\langle l \rangle^{(i)}$. The problem is then to construct one or more of the above distributions given the values of $w^{(i)}$ and $\langle l \rangle^{(i)}$ for all the components.

If the components were essentially monodisperse in mean block lengths a distribution could be constructed unambiguously, but since there is necessarily a distribution of mean block lengths within each component, some assumption about the nature of these distributions must be made. A common method of analyzing fractionation data to obtain molecular weight distributions is to assume that one-half of the weight of a fraction consists of molecules having molecular weights below the average molecular weight and the other half above, or in other words, that the mean and median of the weight distribution of each fraction are equal.[4] If we further assume that the overlap of distributions between the different fractions is sufficiently small that the molecular weights of the material in the ith fraction are between $M^{(i-1)}$ and $M^{(i+1)}$, where $M^{(j)}$ is the molecular weight of the ith fraction, then the cumulative weight distribution is given by

$$C_w(M^{(i)}) = (1/2)w^{(i)} + \sum_{j=1}^{i-1} w^{(j)}$$

where $w^{(i)}$ is the weight of the ith fraction as a fraction of the weight of the original sample and $M^{(i)}$ is the average molecular weight of the ith fraction. The weight density is then obtained by differentiation of this weight distribution treated as a continuous function. We can make a similar assumption for a separation by isotacticity. In the case of isotactic sequence lengths, the average obtained is a number average,[3] however, so the assumption that should be made is that the median of each number distribution is equal to the average as given by $\langle l \rangle^{(i)}$. The cumulative number distribution is then given by

$$C_n(\langle l \rangle^{(i)}) = (1/2)n^{(i)} + \sum_{j=1}^{i-1} n^{(i)} \qquad \text{(A.1)}$$

where $n^{(i)}$ is the number of like-configuration sequences in the ith component as a fraction of the number of blocks in the original sample. Since the $n^{(i)}$ are not measured directly, they must be inferred from the $w^{(i)}$ and $\langle l \rangle^{(i)}$ that are measured.

To derive the relation between $n^{(i)}$ and $w^{(i)}$ and $\langle l \rangle^{(i)}$, we define $N_{\bar{l}}^{(i)}$ as the number of like-configuration sequences in component i in molecules with a mean sequence length $\bar{l}$, so

$$N_{\bar{l}} = \sum_{j=1}^{m} N_{\bar{l}}^{(j)}$$

The number of like-configuration sequences in component i in molecules with a mean sequence length $\bar{l}$ as a fraction of the number of like-configuration sequences in the original sample is then

$$n_{\bar{l}}^{(i)} = N_{\bar{l}}^{(i)} / \sum_{j=1}^{m} \sum_s N_s^{(j)}$$

and the number of like-configuration sequences in the ith component as a fraction of the number of like-configuration sequences in the original sample is

$$n^{(i)} = \sum_{\bar{l}} n_{\bar{l}}^{(i)}$$

The weight of like-configuration sequences in component i in molecules with a mean sequence length as a fraction of the weight of the original sample is

$$w_{\bar{l}}^{(i)} = \bar{l} n_{\bar{l}}^{(i)} / \sum_{j=1}^{m} \sum_s s n_s^{(j)}$$

and the weight of like-configuration sequences in the ith component as a fraction of the weight of the original sample is

$$w^{(i)} = \sum_{\bar{l}} w_{\bar{l}}^{(i)} = \sum_{\bar{l}} \bar{l} n_{\bar{l}}^{(i)} / \sum_{j=1}^{m} \sum_s s n_s^{(j)}$$

The average sequence length of the ith component is

$$\langle l \rangle^{(i)} = \sum_{\bar{l}} \bar{l} n_{\bar{l}}^{(i)} / n^{(i)}$$

so

$$w^{(i)} = \langle l \rangle^{(i)} n^{(i)} / \sum_{j=1}^{m} \langle l \rangle^{(j)} n^{(j)}$$

which yields the set of homogeneous linear equations

$$\sum_{j=1}^{m} (w^{(i)} - \delta_{ij}) \langle l \rangle^{(j)} n^{(j)} = 0 \qquad 1 \le i \le m \qquad \text{(A.2)}$$

where

$$\delta_{ij} = 1 \quad i = j$$
$$= 0 \quad i \neq j$$

which can be solved by standard techniques[21] for the $n^{(i)}$ subject to the normalization condition that

$$\sum_{j=1}^{m} n^{(j)} = 1 \qquad \text{(A.3)}$$

The average sequence length of the original sample is given by

$$\langle l \rangle = \sum_{j=1}^{m} n^{(j)} \langle l \rangle^{(j)}$$

which can serve as a check on the consistency of the data.

Once the $n^{(i)}$ have been calculated from eq A.2 and A.3, the cumulative number distribution can be obtained from eq A.1. The number density, the cumulative weight distribution, and the weight density can then be inferred from this distribution. If we treat the distribution as a continuous function, then

$$n_{\bar{l}} = \mathrm{d}C_n(\bar{l})/\mathrm{d}\bar{l}$$

$$C_w(\bar{l}) = \int_0^{\bar{l}} s C_n(s)\, \mathrm{d}s \Big/ \int_0^{\infty} s C_n(s)\, \mathrm{d}s$$

and

$$w_{\bar{l}} = \mathrm{d}C_w(\bar{l})/\mathrm{d}\bar{l}$$

Registry No. Isotatic poly(1-butene), 25036-29-7; poly(1-butene), 9003-28-5; titanium chloride, 11130-18-0.

Supplementary Material Available: Molecular weight distributions of samples and components, differential scanning

calorimetry curves of samples and components, and X-ray diffraction scan of sample II component 1 (29 pages). Ordering information is given on any current masthead page.

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(22) In this paper the periodic group notation in parentheses is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13–18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

Unusual Anionic Desalting Oligomerization of Alkali Metal Salts of Bromo-Substituted Bicyclic Oxalactam

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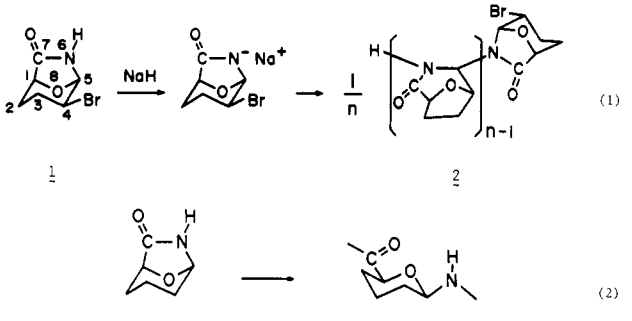
ABSTRACT: The oligomerization of sodium and potassium salts of a new bromo-substituted bicyclic oxalactam, 4(e)-bromo-8-oxa-6-azabicyclo[3.2.1]octan-7-one (**1**), proceeds in *N,N*-dimethylformamide or dimethyl sulfoxide at 0 or 25 °C with elimination of alkali metal bromide to give novel oligomers **2** having a bicyclic oxalactam ring in each monomer unit. Oligomers similarly obtained from mixtures of **1** with its sodium salt had lower average molecular weight. Two diastereomeric dimers and a trimer were isolated by fractional elution from a preparative silica gel column. Structural analyses indicate that the oligomerization proceeds with high enantiomeric selectivity and complete retention of the configuration of the bridgehead methine carbon atom adjacent to nitrogen. Possible mechanisms for this oligomerization are presented.

Introduction

The bicyclic oxalactam 8-oxa-6-azabicyclo[3.2.1]octan-7-one (**3**) can be polymerized anionically at room temperature and dimethyl sulfoxide (Me_2SO) to a high molecular weight polyamide, poly(tetrahydropyran-2(e),6(e)-diyliminocarbonyl) (**4**).[1,2] Polyamide **4** is easily cast to a hygroscopic membrane that has high permeability to water and high permselectivity for aqueous solutes.[1-6] The polyamide is also useful as a component of amphiphilic graft and block copolymers.[7-13] The facile polymerization of **3** must be related to its molecular structure.[1,2,14] The effect of a polar substituent on the reactivity of the bicyclic oxalactam, as in bicyclic acetals,[15-19] is of interest.



(1)

1 **2**

(2)

3 **4**

The anionic polymerization of common lactams generally proceeds through cleavage of the amide bond.[20-23] Recently, X-ray structural analysis of optically active **4** has shown that the anionic polymerization of **3** proceeds with no inversion of configuration of the methine carbon atoms adjacent to oxygen in **3**, indicating that **3** polymerizes through scission of the C–N amide bond. On the other hand, the cationic oligomerization of **3**, which has the structure –OCHNHCO–, proceeds by cleavage of the CH–NH bond,[25,26] while that of some bicyclic lactam ethers involves opening of the ether bond.[27,28] It was therefore of interest to determine whether a nucleophilic reaction of bicyclic oxalactam analogues with the ether–amide bond would involve cleavage of the amide bond.

We have made a preliminary report of the synthesis of a new bicyclic oxalactam, 4(e)-bromo-8-oxa-6-azabicyclo-[3.2.1]octan-7-one (**1**), and of the oligomerization of its sodium salt with elimination of sodium bromide.[29] We here report details of the anionic oligomerization of alkali metal salts of **1** and discuss the oligomerization mechanism as it relates to enantiomeric selectivity and retention of configuration.

Results and Discussion

Preparation of 1. Compound **1** was synthesized from sodium 3,4-dihydro-2*H*-pyran-2-carboxylate (**5**), which is also a starting material for the synthesis of **3** (Scheme I).[1,2]

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