118798-32-6; 1,8-dibromooctane, 4549-32-0; 1-[4-(4′-ethylbiphenyl)]-6-bromohexane, 118798-33-7; 1-[4-(4′-ethylbiphenyl)]-8-bromooctane, 118798-34-8; 1-[4-(4′-butylbiphenyl)]-6-bromohexane, 118798-35-9; 1-[4-(4′-butylbiphenyl)]-8-bromooctane, 118798-36-0; 4-ethyl-4′-bromobiphenyl, 58743-79-6; 1,4-dibromobutane, 110-52-1.

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Thermotropic Hydrocarbon Side-Chain Liquid Crystalline Polymers. 2. Polymer Synthesis and Tacticity

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ABSTRACT: Thermotropic hydrocarbon liquid crystalline α-olefin monomers have been polymerized with $AlEt_3/TiCl_4$ to form high molecular weight polymers. The properties of side-chain liquid crystalline polymers and poly(1-alkene)s are known to be highly dependent on tacticity. The tacticities of the new polymers range from 65% ± 10% to 90% ± 10% isotactic as determined by high-field ^{13}C nuclear magnetic resonance (NMR) spectroscopy. A model system employing poly(1-octadecene) has been used to identify the proper polymerization catalyst for the preparation of atactic liquid crystalline polymers. ^{13}C NMR has been used to show that atactic and isotactic poly(1-octadecene) can be distinguished on the basis of solubility and melting behavior. Preliminary experiments have not been successful in preparing atactic polymers from the new mesogenic monomers.

Introduction

A broad variety and number of side-chain liquid crystalline polymers have been prepared in recent years. Although the tacticities of most of the polymers have not been specified, some workers have studied the influence of backbone stereochemistry on liquid crystalline polymer properties. Newman, Frosini, and Magagnini have shown[1] that the transition temperatures of syndiotactic-rich poly(*p*-biphenyl acrylate) are much higher than the transition temperatures of isotactic polymer. In 1981, Ringsdorf et al. demonstrated[2] that the transition temperatures of a liquid crystalline poly(methacrylate) derivative were also influenced by tacticity.

In 1968, Aubrey and Barnatt reported[3] that poly(1-octadecene) prepared with $Et_3Al/TiCl_4$ catalyst displayed two melting points, 42 and 68 °C. The portion of the polymer soluble in hexane had only one melting point, at 42 °C, whereas the portion insoluble in hexane displayed a melting point of 68 °C. Aubrey and Barnatt proposed that the higher melting fraction was isotactic and the lower melting fraction atactic but offered no direct evidence for the tacticity assignment. In a series of papers, Magagnini and co-workers have investigated[4–7] the influence of tacticity on the side-chain packing of poly(1-eicosene). They used a variety of techniques to show that isotactic and atactic poly(1-eicosene) have different melting points, different crystal structures, and different solubility behavior. Data compiled by Porter, Wang, and Knox show[8] that poly(1-alkene)s with side chains of 11–14 carbon atoms also display two melting points.

The thermotropic hydrocarbon liquid crystalline monomers described in the first paper[9] of this series have been polymerized with Ziegler–Natta catalysts. In the present work, six new hydrocarbon polymers containing biphenyl mesogens in the side chain have been prepared from corresponding mesogenic monomers with a $Et_3Al/TiCl_4$ catalyst. The molecular weights of the six polymers and of a polymer prepared with a different catalyst (described below) have been measured by gel permeation chromatography (GPC), and the tacticities have been determined

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Table I
Yields and Analytical Data for Biphenyl-Containing Polymers

code (formula)	yield, %	calculated, % C	calculated, % H	actual, % C	actual, % H
PEBP04 ($C_{18}H_{20}$)	10	91.47	8.53	91.18	8.69
PEBP06 ($C_{20}H_{24}$)	12	90.85	9.15	90.63	9.21
PEBP24 ($C_{20}H_{24}$)	5	90.85	9.15	90.80	9.29
PEBP26 no. 1 ($C_{22}H_{28}$)	15	90.35	9.65	90.13	9.63
PEBP26 no. 2 ($C_{22}H_{28}$)	36	90.35	9.65	90.13	9.63
PEBP44 ($C_{22}H_{28}$)	12	90.35	9.65	90.13	9.63
PEBP46 ($C_{24}H_{32}$)	8	89.94	10.06	89.97	9.91

by ^{13}C nuclear magnetic resonance (NMR) spectroscopy.

An important long-term objective of this work is to study the effect of tacticity on the liquid crystalline properties of the new polymers. Chien and Kuo have developed a catalyst that has been reported[10] to polymerize 1-propene to 96% isotactic polymer. Accordingly, one new polymer has been prepared with the catalyst used by Chien and Kuo in an effort to prepare a highly isotactic side-chain liquid crystalline polymer. A procedure using 1-octadecene as a model monomer has been developed to identify the proper catalyst for the polymerization of the new monomers to atactic polymers. Attempts to prepare atactic polymer from one of the mesogenic monomers have been unsuccessful thus far. Some of our preliminary data have been reported previously.[11] The liquid crystalline properties of the polymers will be reported in the third paper in this series.

Experimental Section

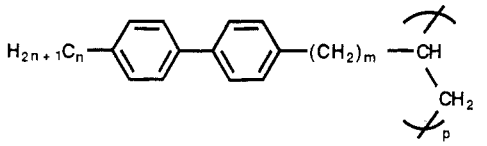
Materials. Chlorobenzene was purchased from Aldrich Chemical Co. and freshly distilled under an Ar atmosphere from $LiAlH_4$ before use. 1-Octadecene was obtained from Aldrich Chemical Co., vacuum distilled from CaH_2, and stored under Ar before use. Triethylaluminum was obtained from Aldrich Chemical Co. as a 1.0 M solution in hexanes and was used without further purification. Titanium tetrachloride was obtained from Aldrich Chemical Co. and was used as received.

A catalyst slurry consisting of $MgCl_2$, ethyl benzoate, *p*-cresol, triethylaluminum, and titanium tetrachloride was kindly provided by Professor J. C. W. Chien of the University of Massachusetts. The slurry will be referred to as the "Chien catalyst". The preparation of the Chien catalyst has been previously described.[12] Methyl-4-methylbenzoate was purchased from Aldrich chemical Co. as a Gold Label product and was dried under vacuum before use.

Preparations. The preparation of poly[6-(4-biphenyl)-1-hexene] is given below. The syntheses of the other five polymers polymerized with $Et_3Al/TiCl_4$ were performed in a similar manner. Since the systematic names of the polymers are awkward, a code system is used to refer to the polymers throughout the Results and Discussion section. For instance, PEBP46 is polyethylene (backbone type) biphenyl (mesogen type), with a tail length of four (in carbon atoms) and a spacer length of six (in carbon atoms). PEBP26 no. 1 was polymerized with $Et_3Al/TiCl_4$, and PEBP26 no. 2 was polymerized with the Chien catalyst. The yields and elemental analyses of the polymers are given in Table I. The generalized structure of the polymers is shown in Table II.

Poly[6-(4-biphenyl)-1-hexene] (PEBP04). 6-(4-Biphenyl)-1-hexene (MEBP04) (2.36 g, 0.01 mol) was placed into a 25-mL single-neck round-bottom flask with a Teflon-coated stir bar. The flask was attached to a vacuum line, degassed, back-flushed with Ar several times, and capped with a septa. Dry chlorobenzene, 10 mL, was added via syringe to produce a clear monomer solution; 1 mL (0.001 mol) of a 1.0 M Et_3Al solution in hexanes was added via syringe to produce a clear solution. Six drops of $TiCl_4$ from a no. 16 syringe needle (about 60 mg, 3×10^{-4} mol) were added to the flask, immediately producing a dark-red suspension. The suspension was stirred at room temperature for 24 h.

Table II
GPC Molecular Weight



code	n	m	M_n	M_w	M_w/M_n
PEBP04	0	4	49 000	450 000	9
PEBP06	0	6	43 000	660 000	15
PEBP24	2	4	26 000	250 000	10
PEBP26 no. 1	2	6	90 000	850 000	9
PEBP26 no. 2	2	6	80 000	380 000	5
PEBP44	4	4	14 000	330 000	24
PEBP46	4	6	70 000	710 000	10

The contents of the flask were poured into 250 mL of ethanol. The white product that precipitated was allowed to coagulate for several hours before removal by filtration. The polymer, which was soluble in hot benzene, was extracted from the precipitate by stirring the precipitate in hot benzene, centrifuging, and decanting the warm, clear benzene solution into 250 mL of ethanol to precipitate the polymer. The process was repeated twice with the newly precipitated polymer to completely remove the material insoluble in hot benzene. Elemental analysis results indicated that the insoluble material was mainly inorganic. The polymer was collected by filtration and dried under vacuum to yield 240 mg of white, fibrous product.

Poly(8-[4-(4′-ethylbiphenyl)]-1-octene) (PEBP26 no. 2). The Chien catalyst is a slurry with a concentration of 39.5 mg of solids/mL of heptane. Titanium comprised 3.5% of the weight of the solids. 8-[4-(4′-Ethylbiphenyl)]-1-octene (MEBP26) (0.585 g, 2×10^{-3} mol) was placed into a 25-mL single-neck round-bottom flask with a stir bar. The monomer was dried for 24 h under vacuum. The flask was septa-capped and flushed with Ar. Chlorobenzene, 2 mL, was added via syringe to produce a clear monomer solution. Et_3Al, 1 M, in hexanes (3.34 mL, 3.34×10^{-3} mol) was added to the flask via syringe. A solution of 167 mg (1.11×10^{-3} mol) of methyl 4-methylbenzoate in 1 mL of chlorobenzene was added to the flask via syringe. Within 2 min, 0.7 mL (0.96 mg of Ti, 2×10^{-5} mol) of the vigorously stirred Chien catalyst was added to the flask via syringe. The resulting brown suspension was stirred at room temperature for 16 h.

The suspension was poured into 50 mL of ethanol, producing a white precipitate. The precipitate was collected by filtration, stirred in hot benzene, and centrifuged, and the clear supernatant was poured into ethanol to precipitate the polymer. The extraction and precipitation process was repeated 3 times, until the portion soluble in hot benzene had been completely removed. Elemental analysis results indicated that the insoluble portion was mainly inorganic material. After vacuum drying, the yield of fibrous white polymer was 210 mg.

Poly(1-octadecene). 1-Octadecene (2.52 g, 0.01 mol) was added via syringe to a 25-mL, septa-capped, Ar-flushed round-bottom flask containing a Teflon-coated stir bar. A 1.0 M Et_3Al solution (1 mL, 0.001 mol) in hexanes was added via syringe to produce a clear solution. Six drops of $TiCl_4$ from a no. 16 syringe needle (about 60 mg, 3×10^{-4} mol) were added to the flask, immediately producing a dark-red suspension. The suspension was stirred at room temperature for 24 h. The contents of the flask were precipitated into 250 mL of ethanol and purified in a manner similar to that described for poly[6-(4-biphenyl)-1-hexene) (PEBP04) to yield 1.54 g of white, fibrous product. Yield, based on monomer weight, was 61%. This sample is designated POCT.

One gram of POCT was placed into a centrifuge tube and stirred with 10 mL of hexane at room temperature. After several hours, the mixture was centrifuged and the clear supernatant poured into 100 mL of ethanol, producing a white precipitate.

Table III
^{13}C NMR Aliphatic Carbon Peak Assignments for Polymers

carbon no.[a]	chemical shift, ppm[b]					
	PEBP04	PEBP06	PEBP24	PEBP26	PEBP44	PEBP46
1	39.9	40.0	39.9	40.0	39.9	40.0
2	32.0	32.2	32.0	32.2	32.0	32.2
3	34.5	34.9	34.5	34.9	34.5	34.8
4	26.3	26.5	26.3	26.5	26.3	26.5
5	32.0	29.7	32.0	29.7	32.0	29.8
6	35.6	30.0	35.7	30.0	35.6	30.2
7		31.6	28.4	31.6	35.3	31.7
8		35.7	15.5	35.7	33.6	35.7
9				28.4	22.4	35.3
10				15.5	14.0	33.6
11						22.4
12						14.0

[a] The numbering system assigns 1 to the backbone methylene carbon, 2 to the backbone methine carbon, and then continues consecutively and progressively down the side chain to the end of the tail. See Figures 1–7. [b] The peak assignments were made for the aliphatic carbons by comparison with known structures and by the use of standard additivity relationships (See ref 13).

More hexane was added to the polymer remaining in the centrifuge tube, and the extraction process was repeated until no precipitate was observed when the supernatant was decanted into ethanol. The hexane-soluble polymer was removed by filtration from the ethanol, dried under vacuum, and weighed to give 290 mg of white polymer, designated POCTS. The hexane-insoluble portion was washed with ethanol, filtered, dried under vacuum, and weighed to give 690 mg of white polymer, designated POCTI. The w/w ratio of hexane-insoluble polymer to hexane-soluble polymer was 70 to 30.

Measurements. Elemental analyses were performed at the Microanalytical Laboratory at the University of Massachusetts. Differential scanning calorimetry (DSC) experiments were performed on a Perkin-Elmer DSC-II at a heating rate of 20 °C/min and a cooling rate of 10 °C/min. The instrument was calibrated with standard samples of indium and naphthalene. To assure that all of the samples had equivalent thermal histories, the results of the second heating scan have been reported throughout. Tacticities were determined by ^{13}C NMR in $CDCl_3$ solvent with tetramethylsilane (0.00 ppm) as an internal standard. A Varian XL-300 instrument operating at 75.43 MHz was used for all of the experiments. The percent of isotactic polymer in each sample was estimated by measuring peak areas and by comparing the spectra to that of poly(1-eicosene) in the literature.[4] A spin inversion recovery experiment was performed to measure T_1 for the peaks used to determine tacticity, and T_1 was found to be less than 200 ms. Since the time between pulses should be at least 10 times larger than T_1, an acquisition time of 0.8 s and a delay time of 2.2 s were used to acquire the spectra. An inverse gated decoupling technique (decoupled only during the acquisition phase) was used to suppress nuclear Overhauser effect (NOE) enhancement. It was found that 5000–10 000 scans of a sample consisting of 150 mg of polymer in 2.35 g of $CDCl_3$ gave the best spectra.

The molecular weights of the polymers were determined by using gel permeation chromatography (GPC). A Waters 201 liquid chromatograph with Ultrastyragel columns was employed to determine the molecular weights relative to polystyrene standards.

Results and Discussion

The GPC molecular weights and polydispersities of the seven mesogenic polymers prepared for this work are shown in Table II. The polymers have high molecular weights and broad molecular weight distributions. The excellent elemental analyses obtained for the polymers indicate that they are relatively pure and do not contain significant amounts of residual catalyst. The polymerization reactions utilizing $Et_3Al/TiCl_4$ proceeded in rather low yields, 5–15%, in spite of the high molecular weights obtained. Polymerization of 1-octadecene with the same catalyst gave yields of 60–70% in repeated experiments, either in bulk or in chlorobenzene solution. The low yields are not due to impurities in the monomer, as polymerization with the Chien catalyst proceeded in 36% yield. A possible explanation for the low yields is that the growing polymer chain coats the catalyst particles, preventing more monomer from diffusing to the catalyst surface. The fact that unreacted monomer is recovered as the byproduct of the polymerization is consistent with this explanation.

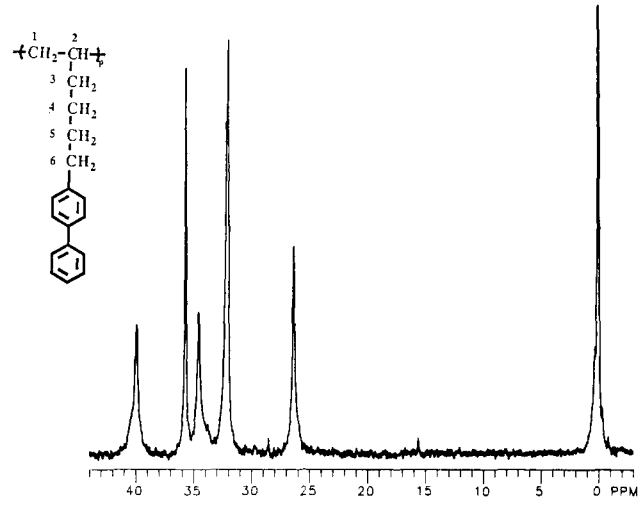


Figure 1. ^{13}C NMR spectrum of PEBP04.

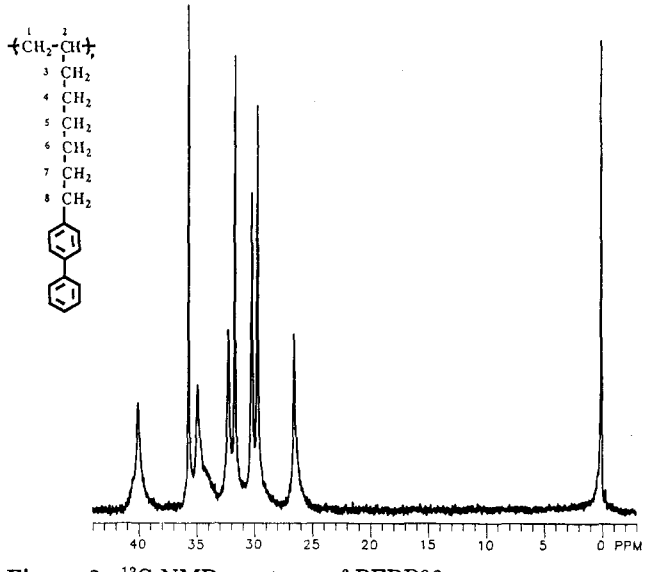


Figure 2. ^{13}C NMR spectrum of PEBP06.

The peak assignments for the aliphatic carbons of the seven mesogenic polymers are shown in Table III. Since PEBP26 nos. 1 and 2 have the same chemical structure,

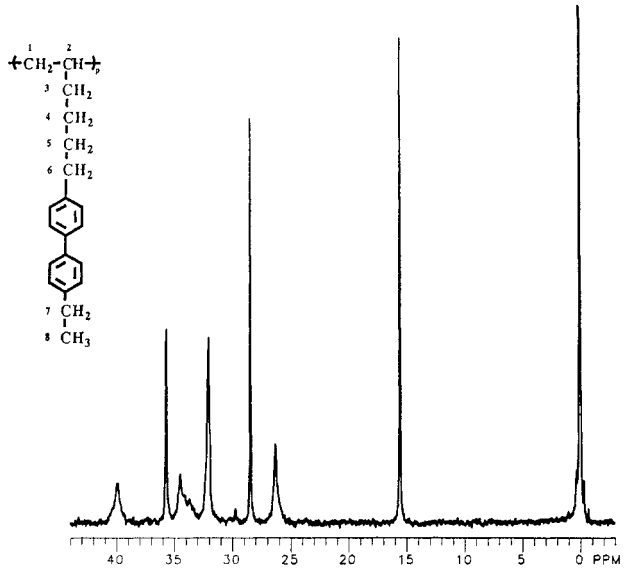


Figure 3. ^{13}C NMR spectrum of PEBP24.

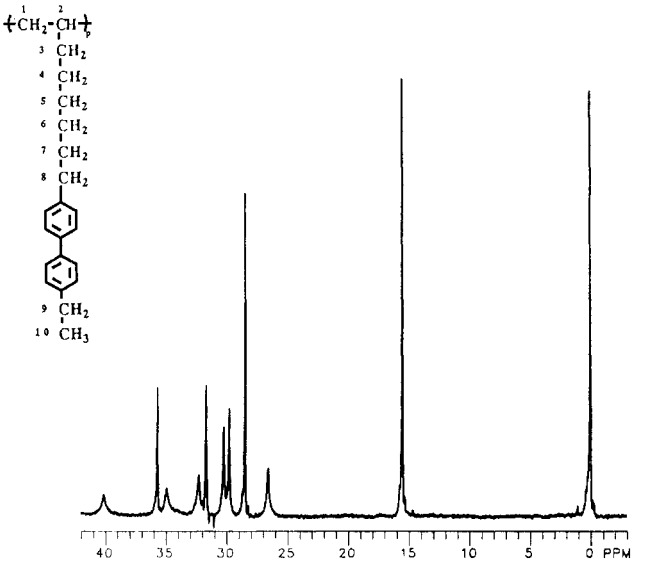


Figure 4. ^{13}C NMR spectrum of PEBP26 no. 1.

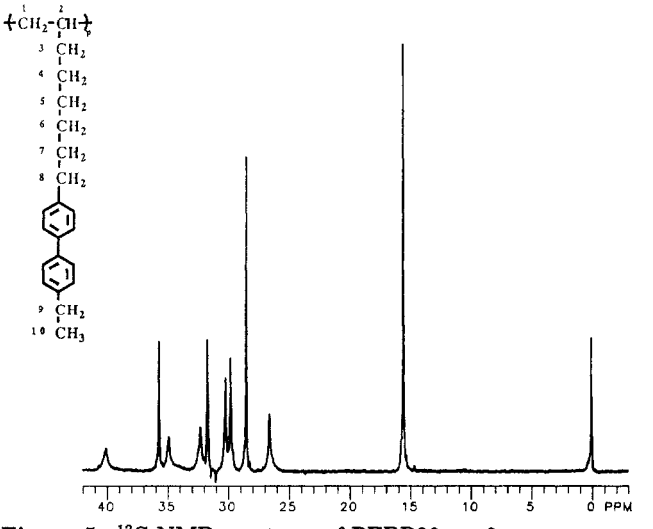


Figure 5. ^{13}C NMR spectrum of PEBP26 no. 2.

the peak assignments for these two polymers have been combined. Figures 1–7 show the ^{13}C NMR spectra obtained for the seven polymers and the method used to number the peaks. The aromatic regions have been

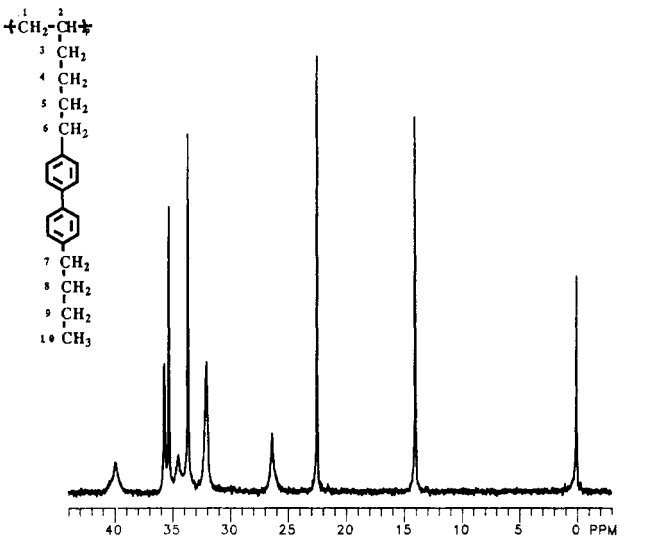


Figure 6. ^{13}C NMR spectrum of PEBP44.

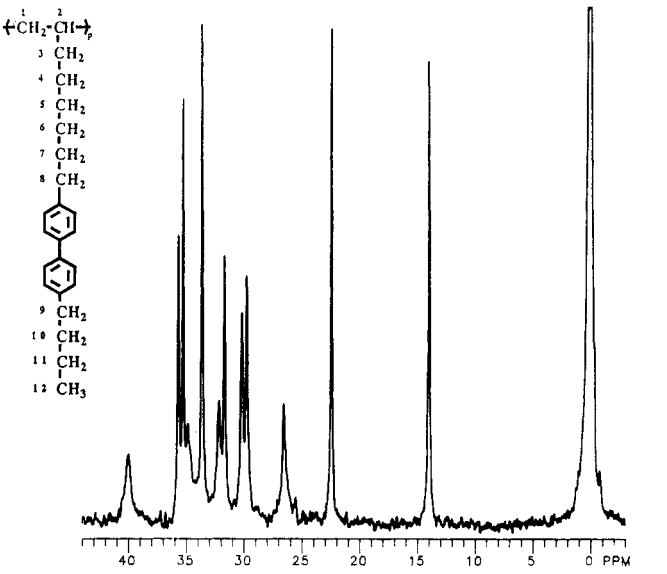


Figure 7. ^{13}C NMR spectrum of PEBP46.

omitted for clarity. The peak assignments were made by comparison with known structures and by the use of standard additivity relationships.[13]

The most useful peak for the assignment of tacticity is peak 1, the backbone methylene carbon peak, because of its sensitivity to tacticity and its relative isolation in the spectrum. Magagnini et al. have also used[4] the backbone methylene carbon to assign tacticity in poly(1-eicosene) samples. The positions of peaks due to carbons 2 and 3, which may also be used to assign tacticity, are obscured by other peaks in the spectra. The chemical shift of the peak 1 occurs at about 40 ppm for all seven of the mesogenic polymers. The ^{13}C NMR spectra of the seven polymers in the 32–42 ppm region are presented on the same scale in Figure 8. The percent isotactic content of each polymer is shown next to the respective spectra. The catalyst $Et_3Al/TiCl_4$ has been reported previously to yield a 50/50 mixture of atactic and isotactic polymers when used to polymerize 1-propene[14] or 1-octadecene.[3] The tacticities of the biphenyl containing polymers prepared in this study ranged from 65% ± 10% to 90% ± 10% isotactic. The high isotactic content of some of the polymers was unexpected. The range of tacticities may be due to the nature of the monomers or to the sensitivity[14] of the catalyst to the particular experimental conditions employed (catalyst ratio, presence of impurities, temperature,

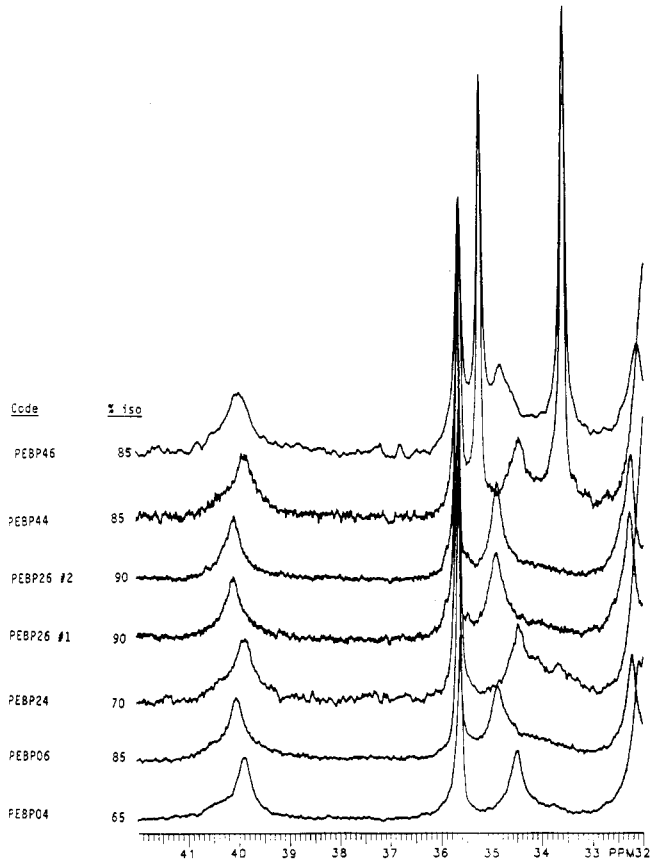


Figure 8. ^{13}C NMR spectra of the seven new mesogenic polymers are shown on the same horizontal scale. The isotactic content of each polymer is shown to the left of the respective spectrum.

solvent, etc.). Duran and Gramain have suggested[15] that biphenyl–biphenyl interactions may influence the tacticity of certain liquid crystalline poly(methacrylate) derivatives. Interactions between the incoming monomer and the chain end or catalyst surface may be responsible for the high isotactic content of the polymers prepared in this work.

PEBP26 no. 2 was prepared with the Chien catalyst, which has been reported[10,12] to yield polymer that is 96% isotactic when used to polymerize 1-propene. The tacticities of PEBP26 no. 1 ($Et_3Al/TiCl_4$ catalyst) and PEBP26 no. 2 were both found to be about 90%, as determined from the 40 ppm peak for both polymers in Figure 8. It is uncertain at this time whether the high isotactic content of the PEBB26 samples is due to the nature of the monomer and/or the nature of the catalyst. In any case, highly isotactic hydrocarbon polymers with mesogenic side chains have been prepared and may be useful for comparison with polymers of differing tacticity.

Since a completely atactic sample of PEBP26 was desired for comparison with the isotactic sample, an effort was initiated to identify catalysts likely to produce atactic long-side-chain poly(1-alkene)s. Because only limited amounts of MEBP26 were available, a model system using 1-octadecene in place of the mesogenic monomer was developed. It was assumed that a catalyst capable of polymerizing 1-ocatadecene to atactic polymer would be a likely candidate for the preparation of atactic mesogenic polymers.

Aubrey and Barnatt[3] have proposed that isotactic and atactic poly(1-octadecene) can be easily distinguished on the basis of solubility and thermal behavior, thus avoiding the rather time-consuming determination of tacticity by ^{13}C NMR. The proposition of Aubrey and Barnatt has been confirmed in the present work by solubility studies, DSC, and ^{13}C NMR. A sample of poly(1-octadecene)

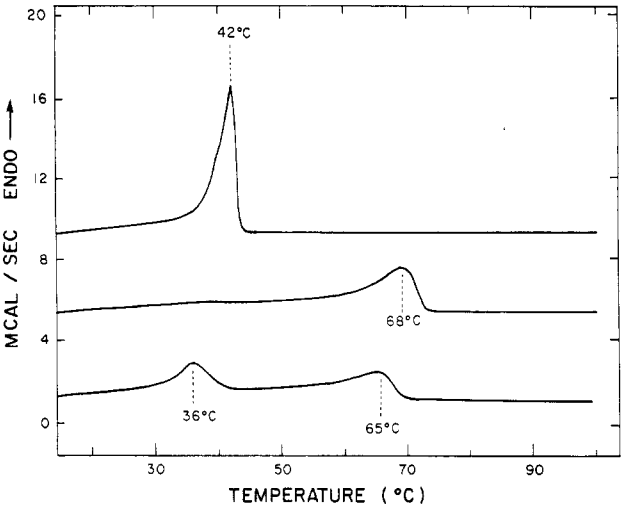


Figure 9. Second heating DSC scans of POCTS (hexane soluble: upper curve), POCTI (hexane insoluble: middle curve), and POCT (unfractionated: lower curve) on the same scale.

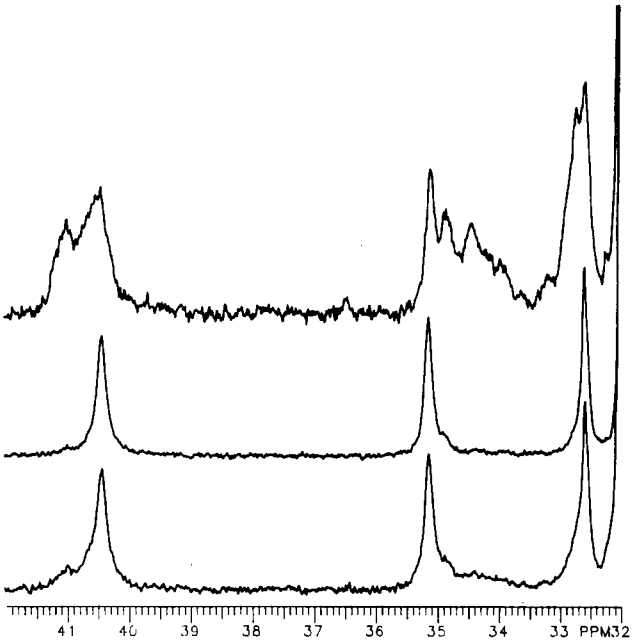


Figure 10. ^{13}C NMR spectra of POCTS (hexane soluble: upper curve), POCTI (hexane insoluble: middle curve), and POCT (unfractionated: lower curve) on the same horizontal scale.

prepared in bulk with $Et_3Al/TiCl_4$ catalyst was extracted at room temperature by *n*-hexane. The w/w ratio of hexane-insoluble polymer to hexane-soluble polymer was 70/30, versus the 50/50 ratio reported by Aubrey and Barnatt. The difference is probably due to the particular experimental conditions employed. The DSC of the hexane-soluble fraction, POCTS, the hexane-insoluble fraction, POCTI, and the unextracted polymer, POCT, are shown in Figure 9. The ^{13}C NMR spectra of the same three polymers are seen in Figure 10. The results clearly show that the unextracted polymer consists of a mixture of atactic and isotactic polymers that independently exhibit their respective melting points. Simple hexane extraction may be used to separate the atactic and isotactic fractions. In this fashion, the tacticity of an unknown poly(1-octadecene) sample may be estimated in a fast, simple, and inexpensive fashion without resorting to ^{13}C NMR. The technique is not quantitative, as the ^{13}C NMR spectrum of the atactic fraction shows the presence of either small amounts of isotactic material or isotactic sequences within the atactic polymer. Low molecular weight

isotactic polymer may be extracted with the atactic polymer into the hexane.

The results are very similar to those obtained[4] by Magagnini et al. for poly(1-eicosene), except for the solvent used to separate the fractions. As mentioned previously, several poly(1-alkene)s with long side chains display two melting points. The work of Magagnini et al. and the present work are in agreement that the two melting points are caused by the presence of atactic and isotactic fractions which independently exhibit their melting points. This suggestion has been confirmed for poly(1-octadecene) and poly(1-eicosene), but further work is needed to establish the nature of the transition in the other polymers.

The soluble Ziegler–Natta catalysts $V(acac)_3/AlEt_2Cl$,[16] Cp_2TiCl_2/methalumoxane, Cp_2ZrCl_2/methalumoxane, and Cp_2HfCl_2/methalumoxane[17–20] were identified as having the potential to polymerize 1-octadecene. So far, we have been unsuccessful in attempts to produce atactic PEBP26 using these catalysts, as only oligomers have been obtained.

Conclusion

A series of six new hydrocarbon side-chain polymers containing the biphenyl mesogen have been prepared with a $Et_3Al/TiCl_4$ catalyst. The polymers have high molecular weights and broad polydispersities. The yields of the polymers were low (5–15%), and unreacted monomer was recovered from the polymerization reactions. A sample of the polymer with a two-carbon tail and six-carbon spacer was also polymerized with the Chien catalyst in 36% yield. The tacticities of the polymers as determined by ^{13}C NMR were shown to range from 65% to 90% isotactic. The isotactic content seemed unusually high and may be due to some specific interaction between the incoming monomer and chain end or catalyst surface.

Aubrey and Barnatt have proposed previously that poly(1-octadecene) prepared with $Et_3Al/TiCl_4$ catalyst is composed of a mixture of atactic and isotactic polymers, which independently display their individual melting points. This suggestion has been confirmed in the present work by separating the isotactic and atactic fractions of poly(1-octadecene) with hexane and determining their tacticities by ^{13}C NMR. The hexane solubility or thermal properties of poly(1-octadecene) may thus be used to establish the tactic preferences of particular catalysts. The two melting points previously reported[8] for poly(1-alkene)s with side-chain lengths of 11–14 carbon atoms are probably due to the independent melting of the atactic and isotactic fractions. Preliminary experiments have not succeeded in finding a catalyst capable of polymerizing one of the new mesogenic monomers to polymers with high atactic content.

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Registry No. PEBP04, 115181-06-1; PEBP06, 115181-08-3; PEBP24, 118798-37-1; PEBP26, 115181-10-7; PEBP44, 115181-12-9; PEBP46, 115181-14-1; MgCl, 7786-30-3; Et_3Al, 97-93-8; $TiCl_4$, 7550-45-0; ethyl benzoate, 93-89-0; *p*-cresol, 106-44-5; poly(1-octadecene), 25511-67-5.

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Preparation and Liquid Crystalline Properties of (Acetyl)(ethyl)cellulose

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ABSTRACT: (Acetyl)(ethyl)cellulose (AEC) samples with a range of acetyl contents were made from (ethyl)cellulose (EC) with a degree of substitution of 2.5. The products formed cholesteric liquid crystals in chloroform, dichloromethane, aqueous phenol, *m*-cresol, dichloroacetic acid, and acetic acid. The acetyl degree of substitution (DS) ranged from 0.0 to 0.5 and strongly influenced the thermal behavior of the polymers in the solid state, with the higher acetyl DS giving higher melting points and heats of fusion. The AEC liquid crystals with high acetyl contents in chloroform, *m*-cresol, aqueous phenol, and acetic acid were right-handed cholesterics, in contrast to the handedness of the original unsubstituted EC in the same solvents. However, in dichloroacetic acid, both AEC and EC were right-handed.

Introduction

Most cellulosic liquid crystals are cholesteric, possessing the exceptionally high optical rotatory power characteristic of the helicoidal supramolecular arrangement.[1–6] The handedness of the mean chain orientation around the helicoidal axis may be deduced from the chiroptical

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