HES, 91742-25-5; CES, 91742-26-6; MS, 1860-17-9; poly(MtA-co-VS), 90168-61-9.

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Optically Active Hydrocarbon Polymers with Aromatic Side Chains. 12. Synthesis and Characterization of Coisotactic Copolymers of (*S*)-4-Methyl-1-hexene with Styrene

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ABSTRACT: The preparation of five styrene/(*S*)-4-methyl-1-hexene copolymer samples in the presence of a stereospecific catalyst [$TiCl_4$/Al(*i*-C_4H_9)$_3$] is reported, and reactivity ratios r_{St} = 0.76 and r_{4MH} = 1.65 have been evaluated for styrene and (*S*)-4-methyl-1-hexene, respectively. The fractionation of the crude copolymerization products by extraction with boiling solvents led to fractions whose chemical composition and relevant spectroscopic characteristics provided qualitative and quantitative information on the distribution of monomer units. This turned out to be completely different from the quasi-random distribution expected from the reported values of the reactivity ratios.

Introduction

Early studies of the copolymerization of a prochiral monomer such as styrene, with an optically active α-olefin by anionic coordinate stereospecific catalysis, led to the synthesis of copolymers characterized by marked induced optical rotation detectable at the level of the aromatic co-units.[1] Accordingly, the potential of this copolymerization method was stressed both with respect to the synthesis of a wide variety of new optically active polymeric materials[2,3] and to the investigation of the chain conformation in solution, by chiroptical techniques.[4,5] To gain a better understanding of the correlation between the circular dichroism of aromatic chromophores and the extent of conformational homogeneity, accurate knowledge of chemical composition, distribution of monomer units, and tacticity are prerequisites to any further speculation on the usefulness of the copolymerization technique and on the polymerization mechanism. While information relevant to the chemical composition of copolymers can be easily achieved by chemical and spectroscopic analysis, only a qualitative measure of the microstructure has been gained by fractionation of the crude polymers with boiling solvents.[2]

The copolymerization of styrene with α-olefins other than propylene has been rather extensively studied since the early sixties and noteworthy are the contributions given in a series of papers by Anderson et al.,[6-9] Overberger and Miyamichi,[10] and Baker and Tait.[11] As a general comment we may stress that the apparent reactivity ratios, reported for copolymerization experiments carried out under different conditions, are affected, other things being equal, by the nature of the catalyst. Moreover, styrene appears to be generally less reactive than linear and far branched α-olefins, whereas with respect to 3-substituted α-olefins styrene displays a marked higher reactivity.

In a previous study[12] on the monomer sequence distribution in copolymers of styrene with chiral α-olefins [(*R*)-3,7-dimethyl-1-octene and (*S*)-4-methyl-1-hexene] prepared in the presence of a VCl_4/Al(*i*-C_4H_9)$_3$ Ziegler–Natta catalyst, a random distribution with some tendency

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Table I
Copolymerization of Styrene (1) with (S)-4-Methyl-1-hexene (2) in the Presence of the Catalytic System Based on $TiCl_4/Al(i\text{-}C_4H_9)_3$

	polymerization conditions[a]			polymeric product		
run	styrene, mmol	molar ratio, 1/2	conv,[b] %	monomeric[c] units from 1, mol %	$[\alpha]^{25}_D$,[d] deg	$[\eta]$,[e] dL/g
C1	34.7	9.00	11.6	87.2	+19	1.9
C2	108.0	3.00	17.8	68.7	+85	3.0
C3	74.3	1.00	22.8	41.4	+138	4.3
C4	75.0	0.30	31.7	15.4	+195	7.2
C5	4.1	0.11	63.2	8.8	+221	7.1

[a] At room temperature in *n*-heptane, molar ratio comonomers/$Al(i\text{-}C_4H_9)_3$ = 9.1 and Al/Ti = 3.3; [1] + [2] = 1.5 mol L^{-1}. [b] Evaluated as (weight of polymer/weight of comonomers) × 100. [c] Evaluated by ^1H NMR and UV spectroscopy. [d] In chloroform. [e] In tetrahydronaphthalene at 120 °C.

to blockiness was observed. Attention has now been directed to a more accurate and satisfying investigation of microtacticity and distribution of monomeric units in copolymers of styrene (1) with (S)-4-methyl-1-hexene (2).

The microtacticity of polystyrene[13,14] and poly[(S)-4-methyl-1-hexene][15,16] obtained by Ziegler–Natta catalysis has been determined by NMR studies, and therefore the copolymers of these monomers appeared to be appropriate for more complete characterization.

In the present paper we wish to report the synthesis of styrene/(S)-4-methyl-1-hexene copolymers, performed in the presence of $TiCl_4/Al(i\text{-}C_4H_9)_3$. The chemical (reactivity ratios and fractionation with boiling solvents) and spectroscopic (UV absorption and fluorescence emission, ^1H NMR and chiroptical techniques) characterization of these copolymers are reported to provide information on the primary structure of the copolymerization product. The analysis of the copolymer microstructure and the relevant considerations concerning the copolymerization mechanism will be discussed in another paper.[17]

Experimental Section

Copolymerization of styrene (1) with (S)-4-methyl-1-hexene (2) having $[\alpha]^{25}_D$ −2.82 (neat), optical purity 93.5%,[18] was carried out in the presence of $TiCl_4/Al(i\text{-}C_4H_9)_3$ as previously reported.[2] Data relevant to the copolymerization experiments are reported in Table I. A typical copolymerization run (run C1) is described here in detail.

A solution of 0.83 g (4.25 mmol) of $Al(i\text{-}C_4H_9)_3$ in 25.8 mL of *n*-heptane was placed in a 100-mL glass vial under dry nitrogen atmosphere and 0.243 g (1.29 mmol) of $TiCl_4$ were slowly added under stirring at room temperature. After 20 min of aging, a mixture of 3.61 g (34.7 mmol) of styrene and 0.382 g (3.9 mmol) of (S)-4-methyl-1-hexene was added and the vial sealed under dry nitrogen. After 15 days the polymerization was interrupted by addition of a large excess of methanol. The coagulated crude polymer was refluxed with methanol containing 1% of concentrated HCl, dissolved in chloroform, and reprecipitated twice into methanol. After drying under vacuum, 0.465 g (11.6% yield) of polymeric product was obtained.

Copolymer samples were fractionated with boiling solvents in Kumagawa extractors[19] using acetone, ethyl acetate, diethyl ether, cyclohexane, and chloroform, in that order (Table II). Viscosity measurements were performed with a dilution viscometer in tetrahydronaphthalene at 120 °C. Optical rotatory measurements were performed on polymer solution in chloroform at 25 °C by a Perkin-Elmer Model 141 spectropolarimeter. Concentrations in the range 0.2–2 g/dL were used. IR spectra were recorded with a Perkin-Elmer 283 B spectrophotometer on polymer films cast from chloroform solution. UV spectra in the range 350–240 nm were recorded at room temperature on polymer solutions in chloroform with a Varian DMS 80 spectrophotometer. Fluorescence emission spectra were obtained with a Perkin-Elmer spectrofluorimeter on polymer solutions in chloroform. Spectra were not corrected for the wavelength dependence of detector response. ^1H NMR spectra were recorded by a Varian XL-100 spectrometer on polymer solutions in $CDCl_3$ using Me_4Si as internal standard.

Table II
Fractionation with Boiling Solvents of Copolymers of Styrene (1) with (S)-4-Methyl-1-hexene (2)

run	fraction[a]	amount, wt %	content of units from 1,[b] mol %	$[\alpha]^{25}_D$,[c] deg	$[\eta]$[d]	$\epsilon_{261}/\epsilon_{262}$[c]	I_E/I_M[c]	1 units in sequence,[e] mol %
C1	I	14.7	90.9	+6	0.16	0.99	n.d.	94
	II	12.1	51.8	+70	n.d.	0.97	0.24	30
	III	0.0						
	IV	0.0						
	V	73.2	96.0	+7	1.7	1.01	0.62	93
C2	I	6.3	80.9	+24	0.16	1.00	0.31	89
	II	30.9	49.0	+100	1.5	0.97	0.18	28
	III	6.0	5.3	+193	3.4	0.97	0.06	<5
	IV	6.0	15.0	+281	5.1	0.96	0.12	<5
	V	50.8	96.0	+7	2.8	0.99	0.70	92
C3	I	4.8	72.3	+43	0.13	0.99	0.34	88
	II	30.5	38.5	+120	1.7	0.97	0.15	17
	III	25.4	3.4	+129	4.6	0.96	0.12	<5
	IV	30.6	1.0	+191	9.4	0.96	0.15	<5
	V	8.7	95.0	+14	3.1	0.99	0.64	90
C4	I	0.7	41.2	+143	n.d.	0.98	n.d.	n.d.
	II	16.3	27.9	+157	1.3	0.97	0.13	10
	III	13.0	4.3	+163	3.3	0.96	0.11	<5
	IV	70.0	2.4	+240	8.8	0.96	0.11	<5
	V	0.0						
C5	I	0.0						
	II	9.0	22.3	+168	0.8	0.97	0.12	<5
	III	27.5	3.3	+175	3.2	0.96	0.06	<5
	IV	63.5	2.4	+277	9.9	n.d.	n.d.	<5
	V	0.0						

[a] Extracted with acetone (I), ethyl acetate (II), diethyl ether (III), cyclohexane (IV), chloroform (V). [b] Determined by UV and ^1H NMR. [c] In chloroform. [d] In tetrahydronaphthalene at 120 °C. [e] Determined by ^1H NMR.

Table III
Mean Sequence Length and Sequence Distribution Data of Copolymers of Styrene (1) with (S)-4-Methyl-1-hexene (2)

run	co-units from 1, mol %	mean sequence length[a] $\bar{l}_1$	mean sequence length[a] $\bar{l}_2$	$X_1(n)$[b] $n=1$	$n=2$	$n=3$	$n=4$	$n\geq 5$	$X_2(n)$[b] $n=1$	$n=2$	$n=3$	$n=4$	$n\geq 5$
C1	87.2	7.75	1.18	1.6	3.0	3.7	4.4	87.3	71.4	22.1	5.1	1.0	0.4
C2	68.7	3.25	1.55	9.4	13.1	13.6	12.5	51.4	41.6	29.5	15.7	7.4	5.8
C3	41.3	1.75	2.65	32.7	28.0	18.0	10.2	11.1	14.2	17.7	16.5	13.7	37.9
C4	15.4	1.22	6.52	66.7	24.4	6.7	1.6	0.6	2.3	3.9	5.0	5.7	83.1
C5	8.8	1.08	15.85	85.2	13.1	1.5	0.1	0.1	0.4	0.7	1.0	1.3	96.6

[a] $\bar{l}_1 = r_1([1]/[2]) + 1$ and $\bar{l}_2 = r_2([2]/[1]) + 1$. [b] Percent fraction of 1 (or 2) units in a close sequence of n.

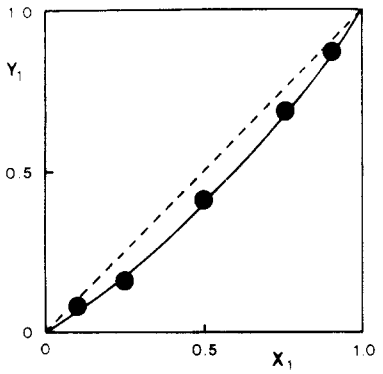

Figure 1. Composition diagram for the copolymerization of styrene with (S)-4-methyl-1-hexene. X_1 and Y_1 are the molar fractions of 1 in the feed and in the copolymer, respectively.

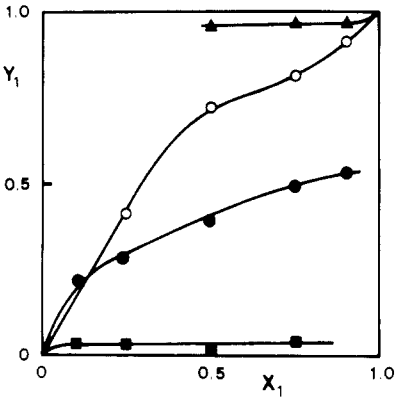

Figure 2. Variation of the composition of fractions of copolymers of styrene with (S)-4-methyl-1-hexene extracted with different solvents, with the feed chemical composition. X_1 and Y_1 are the molar fractions of 1 in the feed and in the copolymer fraction, respectively. ○ acetone (I); ● ethyl acetate (II); ■ diethyl ether (III) and cyclohexane (IV); ▲ chloroform (V).

Results and Discussion

Copolymers of styrene with (S)-4-methyl-1-hexene were prepared in the presence of $TiCl_4/Al(i\text{-}C_4H_9)_3$ catalyst in n-heptane at room temperature using 1/2 molar ratios in the range 9–0.1. The copolymerization experiments were carried out at low conversion (10–30%) with the sole exception of run C5 in which a 63% conversion was obtained. The copolymerization diagram (Figure 1) shows that all the copolymerization products have a higher content of 2 units than the corresponding feed mixture. The reactivity ratios, evaluated by Mayo–Lewis[20] and Fineman–Ross[21] procedures, are in close agreement ($r_1 = 0.76$ and $r_2 = 1.65$) and substantiate the higher reactivity of 2 compared to 1. An opposite behavior ($r_1 = 1.80$ and $r_2 = 1.30$) has been reported for the copolymerization of styrene with racemic 4-methyl-1-hexene performed in the presence of an analogous catalytic system [α-$TiCl_3/Al(i\text{-}C_4H_9)_3$].[7] The product $r_1r_2 = 1.25$, moderately higher than unity, indicates for the investigated samples a substantially random distribution of monomeric units. Average sequence length ($\bar{l}_1$ and $\bar{l}_2$) and mole fraction of 1 and 2 units inserted in sequence of n [$X_1(n)$ and $X_2(n)$] were evaluated by statistical methods from r_1 and r_2 values[22] and are reported in Table III.

It is worth noting that the reactivity ratios, and hence the distribution of monomeric units, have been evaluated under the assumption that the propagation is not controlled by any penultimate effect[23] or any local variation of monomer concentration due to specific monomer interactions in the vicinity of catalytic sites.[9,24,25] This assumption is of general validity in the radically initiated polymerization processes, whereas its extension to either ionic or coordinated heterogeneous polymerization processes does not always seem suitable to describe structural properties of copolymers.[26]

In order to determine if the distribution of monomeric units evaluated by statistical methods corresponds to the real copolymer structure, crude copolymerization products were fractionated according to solubility in different boiling solvents: acetone, ethyl acetate, diethyl ether, cyclohexane, and chloroform, in that order (Table II).

Fractionation occurs according to both molecular weight and chemical composition and gives rise to fractions soluble in acetone and ethyl acetate, consisting mainly of low molecular weight products, and to fractions soluble in cyclohexane and in chloroform, characterized by high molecular weight and containing monomeric units mainly from 2 and 1, respectively. The much lower optical rotation shown by the ethereal fraction (III) with respect to that extracted by cyclohexane (IV) can be attributed to its lower molecular weight or (more likely) to conformational differences induced by a slightly lower configurational homogeneity, as in the case of poly(2).[17,27]

It is interesting to observe that while the relative amount of the various fractions clearly depends on the chemical composition of the initial feed mixture, the composition of fractions soluble in the same solvent does not change very much for the different runs, with the sole exception of fractions extracted by acetone and ethyl acetate (Figure 2).

The presence in most of the copolymerization products of fractions consisting almost exclusively of units derived from one of the two comonomers is clearly in contrast with a quasi-random distribution of monomeric units, as expected on the basis of the reported reactivity ratios.

The various polymer fractions may in principle originate from several independent polymerization processes and therefore the reactivity ratios could be evaluated for each fraction. However, examination of the chemical compositions reported in Table II indicates that fractions III–V contain less than 5% of one monomeric unit and therefore experimental errors in the determination of chemical composition make the reported data unreliable for the evaluation of the reactivity ratios.

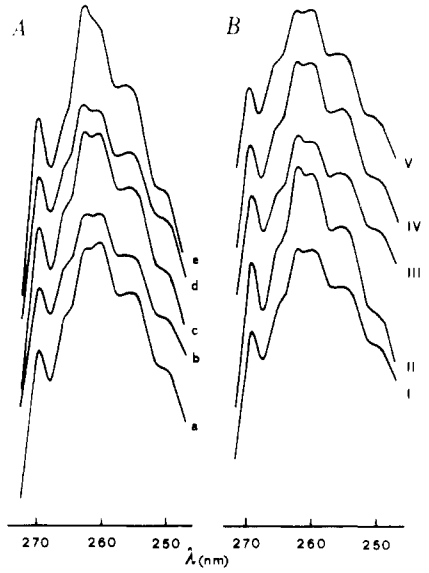

Figure 3. UV spectra in chloroform solution in the 270–250-nm region of A: (a) poly(1), (b) poly(1-*co*-2), run C1, (C) poly(1-*co*-2), run C3, (d) poly(1-*co*-2), run C4, and (e) isopropylbenzene. B: Fractions I–V of poly(1-*co*-2), run C3.

Table IV
Spectroscopic Characterization of Copolymers of Styrene (1) with (*S*)-4-Methyl-1-hexene

sample	monomeric units from 1 (mol %)	$\epsilon_{261}/\epsilon_{262}$[a]	I_E/I_M[a]	mol % of 1 units in sequence: by ^{1}H NMR	mol % of 1 units in sequence: by reactivity ratios
poly(1)	100	1.01	0.77	100	100
C1	87.2	1.00	0.48	86	98
C2	68.7	0.99	0.23	70	91
C3	41.4	0.99	0.22	35	67
C4	15.4	0.98	0.19	8	33
C5	8.8	0.97	n.d.	<5	15
isopropyl-benzene (3)		0.96	0.02		

[a] In chloroform.

The UV spectra of copolymer samples exhibit in the 350–240-nm region a structured absorption band with relative maxima at 269.5, 262.0, 261.0, 256.0, and 251.0 nm, whose intensity profile depends on the content of 1 units. In Figure 3 are reported the UV absorption spectra for three crude copolymer samples, in comparison with polystyrene and isopropylbenzene (3), and the spectra of different fractions derived from the same crude sample.

On increasing the 1 content, the ratio $\epsilon_{261}/\epsilon_{262}$ increases from 0.96 for the low molecular weight structural analogue 3 to 1.01 for isotactic poly(1), it is therefore conceivable that the ratio $\epsilon_{261}/\epsilon_{262}$ gives at least a qualitative measure of the fraction of 1 units in sequence. Such behavior, already observed for polymers containing aromatic chromophores in the side chain,[26,28-31] has been attributed to steric and electronic interactions between neighboring chromophores.[32,33] A complete picture of the trend of the ratio of the molar extinction coefficients at 261 and 262 nm is summarized for crude samples in Table IV, whereas in Table II data are collected for the copolymer fractions. These data, within the limits of the samll range of variability of $\epsilon_{261}/\epsilon_{262}$, seem to indicate that fractions soluble in acetone and in chloroform are characterized by long 1 sequences, whereas in the remaining fractions most of the 1 units should be isolated between 2 units.

Fluorescence emission spectra are characterized by two bands centered at 283.5 and 330 nm (Figure 4) which we attribute to emission from isolated (monomer) and interacting (excimer) chromophores, respectively, by analogy to what has already been reported for polystyrene[34] and for various polymers containing different aromatic chromophores.[28-30,34-36] For unfractionated copolymer samples the intensity ratio of these two bands (I_E/I_M) increases with the content of 1 units up to a maximum value of 0.77 in the case of isotactic poly(1) (Table IV). Taking into account the fact that in polystyrene excimer fluorescence arises only via nearest neighbor chromophore interaction,[37] it is obvious that the ratio I_E/I_M must be related to the relative amount of aromatic units in sequence.

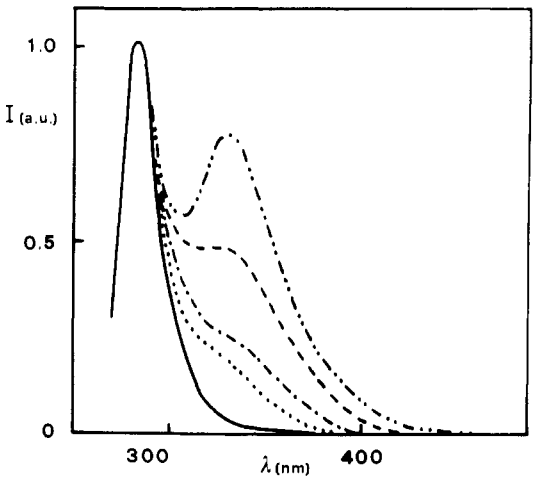

Figure 4. Uncorrected fluorescence emission spectra (chloroform λ_{exc} 258 nm), normalized at the maximum intensity, of (-·-·-) poly(1); (---) poly(1-*co*-2), run C1; (-·-·) poly(1-*co*-2), run C3; (···) poly(1-*co*-2), run C4; (—) isopropylbenzene.

Recently several equations have been proposed to correlate the ratio I_E/I_M with the distribution of monomeric units in copolymers containing fluorescent chromophores.[38-41] However, these relations are still subject to question and do not have general applicability.[42] As a result fluorescence spectra at present can provide only a qualitative picture of comonomer unit sequences. From the analysis I_E/I_M values for the individual fractions (Table II) it is evident that in fractions soluble in diethyl ether and in cyclohexane, aromatic co-units are almost isolated whereas very long sequences of such units are present in chloroform extracts. An intermediate situation can be expected for fractions extractable in ethyl acetate and in acetone.

The ^{1}H NMR spectra of copolymer samples are characterized, in the aromatic region, by a structured band with relative maxima at about 7.2 and 6.7 ppm, whose intensity and shape depend on the content of aromatic units (Figure 5). It has been proposed[43] that in styrene copolymers the aromatic resonance can be deconvoluted in terms of Gaussian and Lorentzian curves, assignable to styrene units inserted in sequences of different length. This assumption, however, does not properly account for any tacticity effect and does not adequately justify the line shape chosen for the deconvolution. Recognizing that the signal at 6.7 ppm has been unequivocally assigned to ortho protons of styrene units inserted in long sequences,[44] it has been possible to evaluate the number of aromatic units in long sequences by graphical deconvolution of the aromatic proton band. This method, however, provides only semiquantitative results for copolymer samples containing a significant proportion of short 1 sequences because of signal coalescence.

The results thus obtained indicate that the fraction of units from 1 inserted in sequence is always lower than that

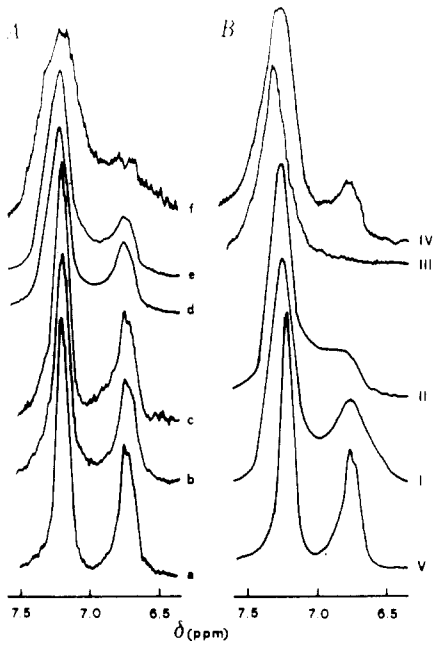

Figure 5. 100-MHz ^{1}H NMR spectra in $CDCl_3$ of A: (a) isotactic poly(1), (b) poly(1-*co*-2), run C1, (c) poly(1-*co*-2), run C2, (d) poly(1-*co*-2), run C3, (e) poly(1-*co*-2), run C4, (f) poly(1-*co*-2), run C5. B: Fractions I–V of poly(1-*co*-2), run C3.

estimated from the reactivity ratios (Table IV). Moreover, in all cases the fractions soluble in acetone and in chloroform contain more than 90% of the aromatic units in sequence, whereas in fractions extracted with diethyl ether and with cyclohexane most of the aromatic units are isolated (Table II).

Analogous indications can be gained from the examination of IR spectra in the 1100–500-cm^{-1} region, where bands connected with the presence of styrene sequences of various length are present.[45] The partial overlapping of the bands of styrene with those of (*S*)-4-methyl-1-hexene makes such estimates at best only qualitative.

Conclusions

The polymerization of mixtures of styrene and (*S*)-4-methyl-1-hexene in the presence of a stereospecific Ziegler–Natta catalyst based on $TiCl_4/Al(i\text{-}C_4H_9)_3$ leads to copolymers characterized by a rather high degree of inhomogeneity in terms of chemical composition, molecular weight, and tacticity.

Fractionation of the crude copolymerization products, mostly isolated at low conversion, allows us to get a better estimate of the complexity of the polymerization process, in that chemical composition, and hence distribution of monomeric units, obtained from the analysis of single fractions, cannot be interpreted on the basis of a mere statistical insertion of the monomers into the growing chain, as one would expect from the comparable reactivity ratios evaluated for the two comonomers (r_1 = 0.76 and r_2 = 1.65). In particular, fractions extracted in acetone (I) and in ethyl acetate (II), having rather low molecular weight and degree of tacticity, very likely do not originate from the highly stereospecific sites typical of Ziegler–Natta catalysts. On the other hand, fractions extracted in diethyl ether (III), cyclohexane (IV), and chloroform (V), containing more than 95 mol % of either aliphatic (III and IV) or aromatic (V) units, consist of highly isotactic, high molecular weight macromolecules and must therefore be grown on the most stereospecific catalytic centers. Spectroscopic properties of fractions III and IV indicate that most of the aromatic 1 units are isolated within long sequences of 2 units. This distribution of monomeric units is in accord with the reported absence of exciton splitting in their CD spectra.[2] In fact, it is well-known that such a splitting originates only from the interactions between neighboring aromatic units imbedded in the asymmetric environment generated by sequences of optically active units.[46]

The reported data further substantiate the previous suggestion[10,11] that the polymerization of styrene and α-olefins occurs at distinct catalytic sites, either preformed or generated in situ by specific interactions of the heterogeneous catalyst with the two electronically and stereochemically differentiated comonomers. However, the spectroscopic techniques employed here can afford only a semiquantitative knowledge of the distribution of 1 units, whereas the distribution of 2 units can be only indirectly deduced, thus limiting the possible mechanistic speculations. A more detailed and accurate description of copolymer microstructure can be gained by a ^{13}C NMR investigation, which will be the subject of a later paper.[17]

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Registry No. Styrene, 100-42-5; (*S*)-4-methyl-1-hexene, 16197-41-4; ((*S*)-4-methyl-1-hexene)·(styrene) (copolymer), 55206-50-3; $TiCl_4$, 7550-45-0; *i*-Bu_3Al, 100-99-2.

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Synthesis of Polyester–Polyether Block Copolymer with Controlled Chain Length from β-Lactone and Epoxide by Aluminum Porphyrin Catalyst

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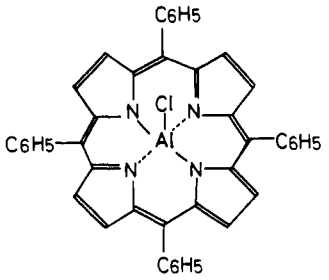
ABSTRACT: (5,10,15,20-Tetraphenylporphinato)aluminum chloride brings about the living polymerization of β-propiolactone and β-butyrolactone to give the corresponding polyester with narrow molecular weight distribution. Polyester–polyether or polyester–polyester block copolymers with narrow molecular weight distribution can be synthesized by adding epoxide or β-lactone as the second monomer to this living polyester. The chain lengths of the blocks can be regulated by changing the amount of the second monomer reacted.

Introduction

We have reported the living polymerization of epoxide such as ethylene oxide, propylene oxide, and 1,2-butene oxide catalyzed by (5,10,15,20-tetraphenylporphinato)-aluminum chloride ((TPP)AlCl, 1) proceeding with an



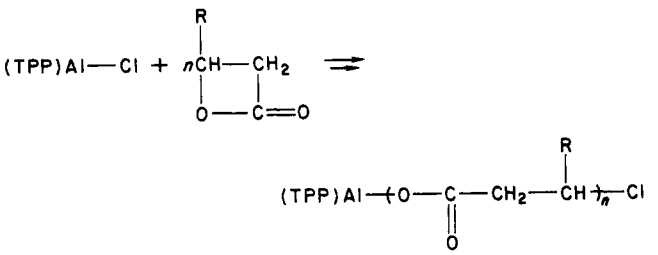
1
TPPAlCl

aluminum alkoxide as propagating end group.[1,2] By the reaction of another epoxide with this living end, polyether–polyether block copolymer can be obtained.[3]

More recently, (TPP)AlCl has been found to exhibit high catalytic activity for the polymerization of β-propiolactone and β-butyrolactone to provide the corresponding polyester with well-controlled molecular weight and narrow molecular weight distribution.[4] The propagating end group in this polymerization has been established to be a (porphinato)aluminum carboxylate[5] (Scheme I).

In the present paper are described further details as to the living nature of the polymerization of β-lactone and its application to the synthesis of block copolymers having polyester–polyether or polyester–polyester sequence with narrow molecular weight distribution. There have been reported so far very limited examples as to the syntheses of polyester–polyether type block copolymer from β-lactone and epoxide[6] and of polyester–polyester type block copolymer from substituted β-lactones,[7] without detailed information about the molecular weight of the products.

Scheme I



Experimental Section

Materials. 5,10,15,20-Tetraphenylporphine ((TPP)H_2) was synthesized by the reaction of pyrrole with benzaldehyde.[8] Diethylaluminum chloride (Et_2AlCl) was distilled under reduced pressure in a nitrogen atmosphere. Dichloromethane, washed with sulfuric acid and then neutralized with sodium bicarbonate, was dried over calcium chloride for 1 night and then fractionally distilled over calcium hydride in a nitrogen atmosphere. β-Propiolactone and β-butyrolactone, dried by stirring with calcium hydride overnight at room temperature, were purified by fractional distillation under reduced pressure in a nitrogen atmosphere over calcium hydride. Ethylene oxide, after stirring with a mixture of potassium hydroxide and calcium hydride at room temperature, was degassed to remove air and then collected in a trap cooled at the liquid nitrogen temperature. Propylene oxide was purified by refluxing over a mixture of potassium hydroxide and calcium hydride and then distilled twice in a nitrogen atmosphere.

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