methacrylates in sulfuric acid and then methylating the resulting acid groups. The degrees of hydrolysis were all less than complete and varied considerably from sample to sample. Since the ease of hydrolysis of *meso* and racemic PMMA differ markedly,[9] it is very probable that the residual ester groups in the methacrylates are also mostly racemic. These residual long chain esters may give similar but slightly different chemical shifts in the triad peaks of the nmr spectra; in addition, side chain ester protons of the longer ester groups may appear in the α-methyl region of the nmr spectra, thereby affecting the apparent stereoregularity of the polymers.

In summary, the hydrogen bonding of the alcohol to the monomeric acid and polyradical appears to be responsible for the solvent effects observed on the stereoregularity of the polymer. The thermodynamic quantities which describe the differences in the transition states for *meso* and racemic addition are consistent with an explanation of the role played by the hydrogen-bonded alcohol upon the stereoregularity of the polymer based on steric effects. In addition, a simple technique is presented for obtaining very highly syndiotactic poly(methacrylic acid); to our knowledge, this polymer containing 95% *rr* triads is the most syndiotactic polymer ever synthesized by radiation polymerization.

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Stereoselectivity and Stereoelectivity in the Copolymerization of Asymmetric Vinyl Ethers

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ABSTRACT: Racemic 1-methylpropyl vinyl ether (I) has been copolymerized with several optically active vinyl ethers, all having an asymmetric carbon atom directly bound to the oxygen atom, in the presence of the stereospecific $Al(O\text{-}i\text{-}C_3H_7)_3$–$H_2SO_4$ heterogeneous catalytic system. When (*S*)-1-phenylethyl vinyl ether (II) or (*R*)-1-phenylethyl vinyl ether (III) or (−)-menthyl vinyl ether (IV) was used as optically active comonomer, the recovered non-polymerized I was optically active, indicating that the process is stereoelective. The chemical composition and the optical rotation of the fractions, obtained by extracting the polymeric product with boiling solvents, showed that the antipode of I, which according to the stereoelective character of the process was polymerized at higher rate, preferentially gives copolymer with the optically active comonomer; the other antipode gives the homopolymer, in agreement with the stereoselectivity of the process. No clear evidence of stereoselectivity was obtained using $BF_3 \cdot O(C_2H_5)_2$ catalyst in homogeneous phase.

Polymerization of racemic 1-methylpropyl vinyl ether (I) in the presence of the stereospecific catalytic system $Al(O\text{-}i\text{-}C_3H_7)$–$H_2SO_4$ was demonstrated to be stereoselective.[1] In fact, the polymer was separated in fractions having optical activity of opposite sign[1] and the degree of separation obtained was larger than that calculated for a statistical copolymer of the two antipodes.[2,3]

This result indicated that active sites {catalytic complex + growing chain end} able to choose between the antipodes of a racemic vinyl monomer[3] can exist in a catalytic system which does not contain transition metals.

On the other hand, the preferential polymerization of one antipode by an optically active catalyst (stereoelective polymerization)[3] has not yet been achieved in the case of vinyl ethers.

Both the stereoselective and the stereoelective characters of the polymerization of α-olefins by Ziegler–Natta catalysts have been clearly confirmed by copolymerizing a racemic monomer with an optically active one.[4] We have, therefore, applied the same type of investigation in order (i) to confirm the stereoselectivity of the polymerization of racemic vinyl ethers by stereospecific catalyst and (ii) to obtain evidence concerning the possible stereoelectivity of the process.

In the present paper we describe the copolymerization of racemic 1-methylpropyl vinyl ether (I) with (*S*)-(II) or (*R*)-1-phenylethyl vinyl ether (III) in the presence of $Al(O\text{-}i\text{-}C_3H_7)_3$–$H_2SO_4$ catalyst. We report the evidence, given both by chemical composition and optical rotation of polymer fractions and by optical rotation of nonpolymerized I, related to the stereoselective and stereoelective character of the process.

The copolymerization of racemic I with (−)-menthyl vinyl ether (IV) is also reported, together with an experiment of copolymerization of I with III carried out in the presence of $BF_3 \cdot O(C_2H_5)_2$.

Experimental Section

(1) Materials. (a) Alcohols. Racemic 2-butanol, bp 99–100°, n^{25}D 1.3951, Erba RP, was used as received. (*S*)-2-

(1) E. Chiellini, G. Montagnoli, and P. Pino, *J. Polym. Sci., Part B*, **7**, 121 (1969).

(2) P. L. Luisi, G. Montagnoli, and M. Zandomeneghi, *Gazz. Chim. Ital.*, **97**, 222 (1967).

(3) P. Pino, F. Ciardelli, and G. Montagnoli, *J. Polym. Sci., Part C*, **16**, 3265 (1968).

(4) F. Ciardelli, C. Carlini, and G. Montagnoli, *Macromolecules*, **2**, 296 (1969).

TABLE I
CHARACTERISTICS OF THE PREPARED OPTICALLY ACTIVE VINYL ETHERS

Starting alcohol[a] Type	Amt, mol	Yield, %	Vinyl ether obtained n^{25}D	$[\alpha]^{25}$D (neat)	Optical purity,[b] %
[(1*R*,3*R*,4*S*)-1-Methyl-4-isopropyl]cyclohex-3-ol {(−)-Menthol}	0.512	89.2	1.4535	−72.2	≥99.0
(+)(*S*)-1-Methylpropanol[c]	0.175	57.4	1.3951	+13.8	95.6
(−)(*S*)-1-Phenylethanol	0.145	69.1	1.5030	−50.3	95.8
	0.098	79.9	1.5030	+46.3	86.9
(+)(*R*)-1-Phenylethanol					
	0.118	73.0	1.5030	+33.9	63.8

[a] If not otherwise indicated, the molar ratios are ethyl vinyl ether–alcohol 20; alcohol–mercuric acetate 11. [b] E. Chiellini and P. Salvadori, to be published. [c] Molar ratio 2-ethylhexyl vinyl ether–alcohol 2; alcohol–mercuric acetate 80.

TABLE II
COPOLYMERIZATION OF RACEMIC 1-METHYLPROPYL VINYL ETHER (I) WITH OPTICALLY ACTIVE VINYL ETHERS IN THE PRESENCE OF $Al(O\text{-}i\text{-}C_3H_7)_3$–$H_2SO_4$[a,b] AND $Al(i\text{-}C_4H_9)_3\cdot THF$[b] AS ACTIVATOR, IN *n*-PENTANE

Run[c]	Optically active comonomer (M_1) Type	$[\alpha]^{25}$D (neat)	Optical purity, wt %	Polymerzn time, hr	Polymzd monomer, wt %	Nonpolymerized monomer (I) $-\alpha^{25}$ (l = 1),[e] deg λ 589	λ 365	$[\alpha]^{25}$D (neat) λ 589	λ 365
B_1	(−)-Menthyl vinyl ether	−72.2	≥99.0	20	50.5	+0.036	+0.070	+0.05	+0.09
B_2	(−)-Menthyl vinyl ether[d]	−72.2	≥99.0	23	9.0	+0.018	+0.035	+0.02	+0.05
B_3	(+)(*R*)-1-Phenyl ethyl vinyl ether	+46.3	86.9	8	38.0	−0.112	−0.204	−0.15	−0.27
B_4	(+)(*R*)-1-Phenylethyl vinyl ether	+33.9	63.8	40	12.0	−0.048	−0.090	−0.06	−0.12
B_5	(−)(*S*)-1-Phenylethyl vinyl ether	−50.3	95.8	18	20.0	+0.114	+0.209	+0.15	+0.27
B_6[f]	(+)(*R*)-1-Phenylethyl vinyl ether	+38.7	72.8	0.7	98.1				

[a] Molar ratio $Al(O\text{-}i\text{-}C_3H_7)_3$–$H_3SO_4$ = 6.83. [b] If not otherwise indicated. [c] Moles of optically active vinyl ether: 2.96×10^{-2} (runs B_1–B_5) and 1.28×10^{-2} (run B_6); molar ratios I/M_1 = 3.0 (runs B_1–B_5) and 5.7 (run B_6), $(I + M_1)/H_2SO_4$ = 185; $(I + M_1)$/activator = 20 (run B_1, B_3–B_5) and 11 (run B_2). [d] Activator $Al(C_2H_5)_3$. [e] Indetermination on the optical rotation ±0.003°. [f] In toluene at −78°, using $BF_3\cdot O(C_2H_5)_2$ as catalyst; molar ratio $I + M_1/BF_3\cdot O(C_2H_5)_2$ = 50.

Butanol, n^{25}D 1.3950, $[\alpha]^{25}$D +13.2 (neat), was obtained by resolution with brucine of the corresponding acid phthalate.[5] (−)-Menthol, Erba F.U., was distilled before use: bp 115° (20 mm); fp 43–44°; $[\alpha]^{25}$D −50.8 (*c* 3.152, ethanol).

(*S*)-1-Phenylethanol and (*R*)-1-phenylethanol were obtained by resolving the corresponding acid phthalate with brucine.[6] A sample of the former had n^{25}D 1.5243 and $[\alpha]^{25}$D −41.0 (neat); two samples of the latter had n^{25}D 1.5242, $[\alpha]^{25}$D +37.2 (neat) and n^{25}D 1.5244, $[\alpha]^{25}$D +26.7 (neat), respectively.

(b) Vinyl Ethers. Ethyl vinyl ether, Erba RP, was distilled over sodium–potassium alloy: bp 35–36°, n^{25}D 1.3745.

Racemic 1-methylpropyl vinyl ether (n^{25}D 1.3951, bp 81–81.5°) and 2-ethylhexyl vinyl ether (bp 76–78° (20 mm)) were prepared by action of acetylene (10–15 atm) diluted with nitrogen (40–45 atm) on the corresponding alcohol in the presence of 10% sodium alcoholate.[7]

(−)-Menthyl vinyl ether, (*S*)-1-methylpropyl vinyl ether, and (*S*)-1-phenylethyl and (*R*)-1-phenylethyl vinyl ether were prepared by transetherification[8] in the presence of mercuric acetate from the corresponding alcohols and either 2-ethyl ethyl or ethyl vinyl ether (Table I).

The purification of the racemic and optically active 1-methylpropyl vinyl ether was carried out as previously reported;[9] the menthyl vinyl ether and 1-phenylethyl vinyl ether were purified by accurate fractional distillation under reduced pressure followed by distillation over $Al(i\text{-}C_4H_9)_3$ (5–10 mol %).

The optical purity of the prepared optically active vinyl ethers was determined by hydrolysis in aqueous acid media to the corresponding alcohols as reported elsewhere[10] (Table I).

(c) Catalysts. $Al(O\text{-}i\text{-}C_3H_7)_3$, BDH, $Al(i\text{-}C_4H_9)_3$, and $Al(C_2H_5)_3$, Texas Alkyls, were purified by distillation under reduced pressure and handled under nitrogen.

The catalyst based on $Al(O\text{-}i\text{-}C_3H_7)_3$ and 100% H_2SO_4 (molar ratio $Al(O\text{-}i\text{-}C_3H_7)$–$H_2SO_4$ = 6.83), and the activator $Al(i\text{-}C_4H_9)_3\cdot THF$ (1:1) were prepared as already reported.[9]

The solvents used for the polymerization experiments and for the fractionation of the polymers obtained were purified by the usual procedures.

(2) Copolymerization Experiments. (a) By $Al(O\text{-}i\text{-}C_3H_7)_3$–$H_2SO_4$ Catalyst (Table II). A mixture of 4.4 g (2.96×10^{-2} mol) of (*R*)-1-phenylethyl vinyl ether and of 8.88 g (8.88×10^{-2} mol) of (*RS*)-1-methypropyl vinyl ether was

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(6) E. Downer and J. Kenyon, *J. Chem. Soc.*, 1156 (1939).
(7) W. Reppe, *Justus Liebigs Ann. Chem.*, **601**, 97 (1956).
(8) W. H. Watanabe and L. E. Conlon, *J. Amer. Chem. Soc.*, **19**, 2828 (1957).
(9) (a) P. Pino, G. P. Lorenzi, and E. Chiellini, *Ric. Sci.*, **34**, 193 (1964); (b) G. P. Lorenzi, E. Benedetti, and E. Chiellini, *Chim. Ind.* (Milan), **46**, 1474 (1964); (c) P. Pino, G. P. Lorenzi, and E. Chiellini, *J. Polym. Sci., Part C*, **16**, 3279 (1969).
(10) See Table I, footnote *b*.

TABLE III
FRACTIONATION AND OPTICAL ACTIVITY[a] OF VINYL ETHERS HOMOPOLYMERS OBTAINED BY $Al(O\text{-}i\text{-}C_3H_7)\text{–}H_2SO_4$ CATALYTIC SYSTEM[b] AND $Al(i\text{-}C_4H_9)_3\cdot THF$ ACTIVATOR

Run	Monomer: Type	Monomer: Optical purity,[d] %	Conversion,[e] %	Polymer fractions extracted successively with boiling methanol and acetone (1–2), diethyl ether (3), benzene (4): 1–2 Wt, %	1–2 $[\alpha]^{25}D$	3 Wt, %	3 $[\alpha]^{25}D$	4 Wt, %	4 $[\alpha]^{25}D$
A_1	(+)(*S*)-1-Methylpropyl vinyl ether (V)	95.6	43.8	8.5	+185	61.9	+234	30.5	+285
A_2	(*RS*)-1-Methylpropyl vinyl ether (I)	0	41.1	21.9		61.4		16.7	
A_3	(−)-Menthyl vinyl ether (IV)	≥99	1.0	27.0	−97.1	73.0	−198	Traces	n.d.
A_4[c]	(+)(*R*)-1-Phenylethyl vinyl ether (III)	86.9	39.5	100.0	+ 70.1				

[a] In benzene. [b] If not otherwise indicated; molar ratio $Al(O\text{-}i\text{-}C_3H_7)_3\text{–}H_2SO_4 = 6.83$. [c] By a catalytic system based on $BF_3O(C_2H_5)_2$ and $Al(i\text{-}C_4H_9)_3$; molar ratio $Al(i\text{-}C_4H_9)_3\text{–}BF_3\cdot O(C_2H_5)_2 = 2.8$. [d] See Table I, footnote *b*. [e] On the basis of the weight of the polymer insoluble in methanol at room temperature.

introduced (run B_4) under nitrogen in a round-bottomed three-necked flask containing 100 ml of *n*-pentane.

After cooling at about −15° (mixture ice–salt) 1.60 g (5.92×10^{-3} mol) of $Al(i\text{-}C_4H_9)_3\cdot THF$, and under vigorous stirring, 2 ml (2.2×10^{-4} mol of 100% H_2SO_4) of catalytic slurry [$Al(O\text{-}i\text{-}C_3H_7)_3\text{–}H_2SO_4 = 6.83$ in isooctane] was introduced.

The reaction mixture was kept 2 hr at −15° and then 38 hr at room temperature (20–25°) under stirring. The polymerization was interrupted by adding 50 ml of methanol containing 2 ml of 16 *M* aqueous ammonia.

The polymer was coagulated with a large excess of methanol and 1.58 g of polymeric products, insoluble in methanol at room temperature, was obtained by centrifugation.

The nonpolymerized 1-methylpropyl vinyl ether was distilled as an azeotropic mixture with methanol, pentane, and traces of isooctane; the distillation (using a Todd glass-ring-packed column 1.50 m long with a section of 3 cm^2) was stopped when the distilling liquid (methanol) did not contain a detectable amount of vinyl ether as tested by gas chromatography using a Perkin-Elmer Model 154/B chromatograph equipped with a 4-m propylene glycol stearate on Celite packed column.

The distilled mixture, separated from methanol by washing with a cold dilute sodium carbonate solution, was dried on $MgSO_4$ and distilled in the presence of sodium–potassium alloy; 8.12 g of distillate containing mainly *n*-pentane (≃75%) and 1-methylpropyl vinyl ether (≃25%), as tested by gas chromatography, was thus obtained.

Using a preparative Perkin-Elmer Model F 21 gas chromatograph equipped with a 5-m column packed with butandiol succinate 8P-51.83 on Chromosorb (A 45/60 mesh) at 130° and with nitrogen as gas carrier (310 ml/min), 1.21 g of pure 1-methylpropyl vinyl ether was obtained from the reported amount having $n^{25}D$ 1.3950, α^{25}_{589} (l = 1) −0.048°, and α^{25}_{365} (l = 1) −0.090° (neat), as measured by a Perkin-Elmer polarimeter, Model 141.

Runs B_2, B_3, and B_5 were carried out in a similar way. In run B_1, the racemic monomer was dropped into the polymerization mixture containing the optically active monomer, the activator, and the catalyst.

The homopolymerization experiments (runs A_1–A_4) (Table III) were performed similarly to run B_4.

(b) By $BF_3\cdot O(C_2H_5)$ Catalyst (Run B_6). A mixture of 7.36 g (7.36×10^{-2} mol) of (*RS*)-1-methylpropyl vinyl ether ($n^{25}D$ 1.3950, bp 81–81.5°) and 1.90 g (1.28×10^{-2} mol) of (*R*)-1-phenylethyl vinyl ether ($n^{25}D$ 1.5032, with 71.4% optical purity), dissolved in 40 ml of anhydrous toluene, was added in 30 min, under nitrogen and vigorous stirring, to a solution of 0.22 ml (1.72×10^{-3} mol) of $BF_3\cdot O(C_2H_5)_2$ in 80 ml of toluene, contained in a three-necked cylindric flask cooled at −78°.

Ten minutes after the addition of monomer mixture, the polymerization was interrupted by addition of 50 ml of methanol containing 2 ml of 16 *M* aqueous ammonia cooled to −78°. A 9.08-g sample of polymer, precipitated by an excess of methanol, was obtained.

(3) Polymer Characterization. The solid polymer was fractionated, after repeated washing with methanol at room temperature, by extraction with boiling solvents (methanol, acetone, diethyl ether, and benzene, in that order) under nitrogen, in Kumagawa extractors.[11]

Extraction with each solvent was stopped when 10–20 ml of percolating liquid did not leave a weighable residue after solvent evaporation. Optical rotation measurements were carried out by a Schmidt–Haensch–Lippich polarimeter with sensitivity ±0.005°, or with a Perkin-Elmer Model 141 polarimeter with sensitivity ±0.003°. Aromatic hydrocarbon solutions having concentration in the range 0.5–5 g/dl were used.

The composition of polymer fractions was determined by nmr or uv spectroscopy (runs B_3–B_6).

Nmr spectra were performed by a Varian DA-60-IL spectrometer equipped with integrator. Solutions of the polymer samples in CCl_4 (*c* 10–25 g/dl), containing hexamethyldisiloxane as internal standard and a weighed amount of 1,1,2,2-tetrachloroethane (*c* 5–25 g/dl), were used. The areas of the peaks centered at 7.15 and 5.80 ppm, characteristic of benzene ring and *sym*-tetrachloroethane protons, respectively, were determined by integration; their relative ratio gives the composition of copolymer samples. The measurements were reproducible up to ±1%.

Uv spectra were performed using a Cary 14 spectrophotometer in the range between 300 and 240 nm. The content of phenyl groups in the copolymer fractions was determined by comparing their absorbance at 258 nm in chloroform solution with that of a solution with a known amount of poly[(*R*)-1-phenylethyl vinyl ether] in the same solvent.

Results

Racemic 1-methylpropyl vinyl ether (I) was copolymerized with (−)-menthyl vinyl ether (IV), (−)(*S*)-1-phenylethyl vinyl ether (II), and (+)(*R*)-1-phenylethyl vinyl ether (III) in the presence of $Al(O\text{-}i\text{-}C_3H_7)_3\text{–}H_2SO_4$ catalytic system and with $Al(i\text{-}C_4H_9)_3\cdot THF$ as

(11) P. Pino, G. Montagnoli, F. Ciardelli, and E. Benedetti, *Makromol. Chem.*, **93**, 198 (1966).

TABLE IV

PHYSICAL PROPERTIES OF FRACTIONS OBTAINED BY EXTRACTING WITH BOILING SOLVENTS THE POLYMERIC PRODUCTS PREPARED BY COPOLYMERIZING (*RS*)-1-METHYLPROPYL VINYL ETHER (I) WITH (−)-MENTHYL VINYL ETHER (IV)

Fractions extracted successively with boiling	Run B_1 Wt, %	Run B_1 $[\alpha]^{25}D^a$	Run B_2 Wt, %	Run B_2 $[\alpha]^{25}D^a$
1 Methanol	4.2	−24.1	4.0	−29.0
2 Acetone	20.0	−19.2	8.0	−46.6
3 Diethyl ether	70.4	−13.4	86.3	−53.4
4 Benzene	5.4	+2.5[b]	1.4	+7.3[b]

[a] In benzene solution, by a Schmidt–Haensch polarimeter (*c* 1.7–3.7 g/dl), if not otherwise indicated. [b] By a Perkin–Elmer Model 141 polarimeter: $[\alpha]^{25}_{365}$ +6.7 (*c* 1.05 g/dl; run B_1) and $[\alpha]^{25}_{365}$ +19.4 (*c* 0.327 g/dl; run B_2).

rotation, as does the homopolymer of IV[12] (Table III; run A_3). The difference in absolute value of the optical rotation of the first three fractions in the two runs could be attributed in principle to a remarkably different conversion to polymeric products (Table II). In fact, the fourth fraction, which has positive optical rotation with a higher value in run B_2, is present in smaller amount in the same run and for this fraction the product of the weight per cent by optical rotation is very similar in both runs B_1 and B_2 (Table IV). Although the chemical composition of the fractions was not determined in this case, the presence of a polymer fraction not extractable with boiling diethyl ether and having positive optical rotation demonstrates the formation of homopolymer of I having a predominantly *S* absolute configuration,[9] which is contained in the fraction considered.

In all experiments involving copolymerization of racemic 1-methylpropyl vinyl ether (I) with (*S*)- (II)

TABLE V

PROPERTIES OF FRACTIONS OBTAINED BY EXTRACTING WITH BOILING SOLVENTS THE POLYMERIC PRODUCTS OBTAINED BY COPOLYMERIZING (−)(*S*)-1-PHENYLETHYL VINYL ETHER (II) OR (+)(*R*)-1-PHENYLETHYL VINYL ETHER (III) WITH RACEMIC 1-METHYLPROPYL VINYL ETHER (I) BY $Al(O\text{-}i\text{-}C_3H_7)_3$–$H_2SO_4$ CATALYTIC SYSTEM (RUNS B_3, B_4, AND B_5) AND BY $BF_3\cdot O(C_2H_5)_2$ (RUN B_6)

	Polymer fractions extracted successively with boiling methanol (1), acetone (2), diethyl ether (3), and benzene (4)											
	1			2			3			4		
Run[a]	Wt, %	Mol %[b] of III or II	$[\alpha]^{25}D^c$	Wt, %	Mol %[b] of III or II	$[\alpha]^{25}D^c$	Wt, %	Mol % of III or II	$[\alpha]^{25}D^c$	Wt, %	Mol %[d] of III or II	$[\alpha]^{25}D^c$
B_3	7.4	22.0	+19.8	77.4	20.5	+28.3	12.8	10.0	+26.1	2.4	1.7	−123.0
B_4	15.6	18.5	+18.4	63.2	19.0	+18.3	20.4	11.0	+20.4	0.8	4.6	−30.6
B_5	8.4	27.3	−29.5	67.3	18.5	−28.7	23.9	16.6	−34.9	0.4	7.2	+53.6
B_6	1.8	14.0	+29.0	89.6	15.0	+32.7	8.6	13.0	+28.6			

[a] Optical purity of III, 86.9% (run B_3), 63.8% (run B_4), and 72.8% (run B_6); and of II, 95.8% (run B_5). [b] By nmr spectroscopy if not otherwise indicated. [c] In benzene (*c* 0.5–5.0 g/dl). [d] By uv spectroscopy.

activator with molar ratio, R_m, racemic monomer M_2 to optically active monomer M_1 3.0.

The molar ratio of monomers (optically active M_1 + racemic M_2) to H_2SO_4 and monomers to activator were the same in all experiments, being 185 and 20, respectively. In run B_2, $Al(C_2H_5)_3$ was used as activator with $(M_1 + M_2)/Al(C_2H_5)_3 = 11$ (Table II). In all the above experiments the recovered nonpolymerized I, racemic at the start, turned out to be optically active, the sign of the optical rotation being opposite to that of the optically active comonomer (Table II).

The solid polymeric products, insoluble in methanol at room temperature, were fractionated by solvent extraction; boiling methanol, acetone, diethyl ether, and benzene were used, in that order, for both homopolymers (Table III) and copolymers (Table IV and V).

The content of monomeric units derived from each comonomer in the extracted fractions was determined by nmr or uv spectroscopy (runs B_3–B_6). No attempt to determine this composition was made in runs B_1 and B_2.

In the copolymerization of racemic 1-methylpropyl vinyl ether (I) with (−)-menthyl vinyl ether (IV) (runs B_1 and B_2), the first three fractions have negative optical

or (*R*)-1-phenylethyl vinyl ether (III) in the presence of $Al(O\text{-}i\text{-}C_3H_7)$–$H_2SO_4$ catalyst (runs B_3–B_5), the polymeric products obtained contain a larger amount of units from I than the starting monomer mixture. The lower reactivity of II (or III) with respect to I is confirmed by the fact that the former monomer does not homopolymerize in the presence of the above-mentioned catalyst. Taking into account this result, as well as the distribution of units from II and III in the different fractions (Table V), and comparing the copolymer fractionation data with the results obtained for the two homopolymers (Table III), the formation of copolymer can be reasonably assumed.[13] As expected from the solvent extraction of the two homopolymers, the content of units from II (or III) decreases in the successive fractions and the fraction extracted with benzene contains more than 90% of units from I (Table V).

In runs B_3 and B_4, in which I was copolymerized

(12) A. M. Liquori and B. Bispisa, *Chim. Ind.* (Milan), **48,** 1045 (1966).

(13) (a) M. F. Shostakovski, A. M. Khomutov, and A. P. Alimov, *Izv. Akad. Nauk SSSR*, 1848 (1964); (b) A. M. Khomutov and A. P. Alimov, *Vysokomol. Soedin.*, **6,** 1068 (1966).

TABLE VI
RELATIONSHIP BETWEEN ABSOLUTE CONFIGURATION OF THE NONPOLYMERIZED 1-METHYLPROPYL VINYL ETHER INITIALLY RACEMIC AND THAT OF OPTICALLY ACTIVE MONOMER

Optically active monomer			Nonpolymerized 1-methylpropyl vinyl ether	
Type	Sign of optical rotation	Abs confign of the asymmetric carbon atom bound to the ethereal oxygen	Sign of optical rotation	Abs confign
1-Phenylethyl vinyl ether	−	*S*	+	*S*
	+	*R*	−	*R*
Menthyl vinyl ether	−	*R*	+	*S*

with III and R_m is 3, the first three fractions have a very similar positive rotation; the last fraction has in both cases negative optical activity but is larger in absolute value in run B_3 where the used sample of III had a larger optical purity. This fraction must therefore contain almost exclusively homopolymer of I, having a predominantly *R* absolute configuration. The same result was obtained in run B_5 in which II was copolymerized with I; in this case the configuration of the optically active comonomer II was *S*, and so, was opposite to that of runs B_3 and B_4. The first three polymer fractions have, therefore, negative optical activity, as does the homopolymer of II, and the last fraction has positive optical activity, as does poly[(*S*)-1-methylpropyl vinyl ether].

Finally, in the copolymerization of I with III (R_m = 5.7) by $BF_3 \cdot O(C_2H_5)_2$ catalyst in a homogeneous phase, a polymeric product, completely extractable with diethyl ether, was obtained. The optical rotation of the fractions is positive here, as it was for the homopolymers of II; the values of optical rotation as well as the composition are very similar for the three fractions (Table V).

Taking into account the large conversion value (98.2%) calculated as weight of polymer insoluble in methanol at room temperature to weight of comonomers mixture, no appreciable amount of nonpolymerized I was recovered, thus preventing a check of its optical activity.

Discussion

The results obtained in the present investigation may be better discussed if stereoelectivity and stereoselectivity of the polymerization process are treated separately. Despite the fact that the data unequivocally show both stereoelective and stereoselective character in the heterogeneous stereospecific $Al(OR)_3$–(H_2SO_4) catalyst, the quantitative aspects are less clear, being influenced by several parameters in a way which is not entirely simple. Therefore, only a rough attempt can be made to interpret the mechanism of the steric features of the process and their correlation with stereoregulation.

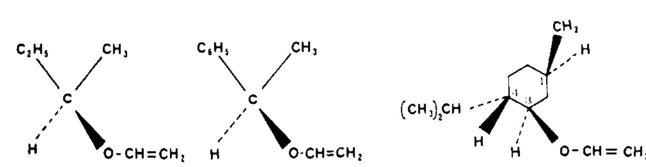
(a) Stereoelectivity. The preferential polymerization of one antipode of the racemic comonomer M_2 has been clearly demonstrated by copolymerizing racemic 1-methylpropyl vinyl ether (I) with (−)-menthyl vinyl ether (IV), as well as with (−)-(*S*)- (II) or (+)-(*R*)-phenyl ethyl vinyl ether (III).

In fact, in these cases the nonpolymerized 1-methylpropyl vinyl ether turned out to be optically active, the sign of its optical rotation being opposite to that of the optically active comonomer M_1 (Tables II and VI).

Since the asymmetric carbon atom bound to the oxygen atom in (−)-menthyl vinyl ether has *R* absolute configuration,[12,14] and the (+)-(1-methylpropyl) vinyl ether has *S* absolute configuration,[9,10] the above result indicates that (−)(*R*)-1-methylpropyl vinyl ether has been incorporated in the polymer product at a higher rate than the *S* antipode.

On the other hand, when (1-phenylethyl) vinyl ether was used as the optically active comonomer, the opposite took place. In fact the − antipode of this monomer has *S* absolute configuration,[10,15] and in its presence (−)(*R*)-1-methylpropyl vinyl ether has been again preferentially polymerized (Table II and VI). In the monomers considered, the spatial arrangement of the groups bound to the asymmetric carbon atom in the α position to the oxygen atom is the same when the above asymmetric atom has the same absolute configuration (Chart I). Therefore

CHART I



(−)(R) I (+)(R) III (−)(1R:3R:4S) IV

no simple relationship exists between the absolute configuration of M_1 and the preferentially polymerized antipode of M_2.

A quantitative evaluation of the stereoelectivity achieved requires the determination of the relative rate (R_p)[4,16] of the antipodes of racemic 1-methylpropyl vinyl ether and can be made only in the polymerization of I with II and III in which the chemical composition of polymer fraction has been determined and, therefore, the conversion C_{M_2} of I to polymeric

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(16) $R_p = (100 + P_p)/(100 - P_p)$ where $P_p = P_n[(100 - C_{M_2})/C_{M_2}]$; P_p = optical purity of polymerized I; P_n = optical purity of nonpolymerized I; C_{M_2} = conversion of I to polymeric products.

TABLE VII
RELATIVE POLYMERIZATION RATE OF THE ANTIPODES OF RACEMIC 1-METHYLPROPYL VINYL ETHER (M_2) IN THE PRESENCE OF OPTICALLY ACTIVE 1-PHENYLETHYL VINYL ETHER (M_1)

Run	Optically active 1-phenylethyl vinyl ether (M_1) Optical purity, %	Abs confign	Molar ratio M_2/M_1	Conversion of M_2,[a] %	Abs confign of nonpolymerized M_2	Optical purity of M_2, % Nonpolymerized (P_n)	Polymerized[b] (P_p)	Relative polymerzn rate[c] (R_p)
B_3	86.9	*R*	3.0	42.5	*R*	1.03	1.39	1.028
B_4	63.8	*R*	3.0	13.7	*R*	0.43	2.70	1.055
B_5	95.8	*S*	3.0	24.3	*S*	1.03	3.20	1.066

[a] Conversion of M_2: $C_{M_2} = C_T[(100 - a_{M_1})/b_{M_2}]$ where a_{M_1} = weight per cent of M_1 in the polymer; b_{M_2} = weight per cent of M_2 in the starting monomers mixture; C_T = total weight of the polymer divided by weight of monomers mixture. [b] $P_p = P_n[(100 - C_{M_2})/C_{M_2}]$. [c] $R_p = (100 + P_p)/(100 - P_p)$.[16]

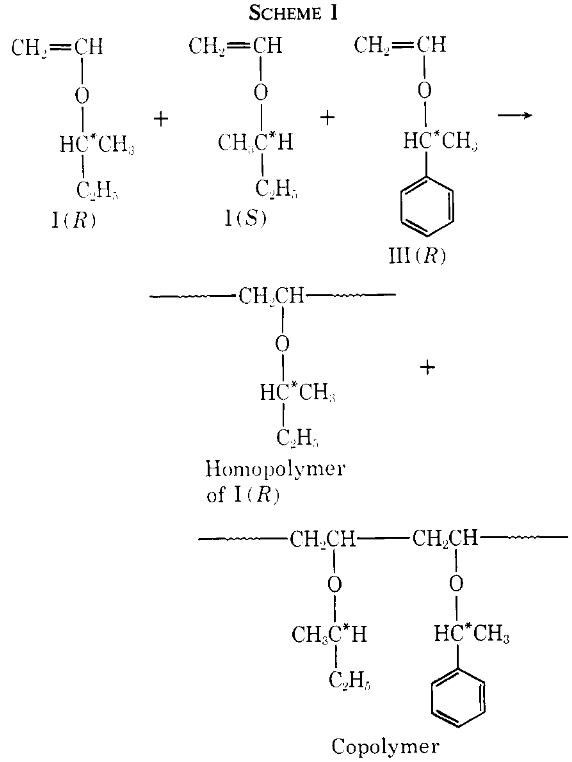
products can be calculated. As demonstrated in Table VII, the optical purity of polymerized I goes from 1 to 3%, and the corresponding value of the relative polymerization rate of the two antipodes (R_p) are 1.02–1.07. Despite the small values of R_p, which could have been affected by small experimental errors and the limited number of experiments, it seems that R_p increases with increasing optical purity of the optically active comonomer (Table VII).

(b) Stereoselectivity. In the same experiments in which stereoelectivity is clearly demonstrated, the optical rotation of the polymer fractions and their chemical composition unequivocally show that the process is stereoselective. In fact, the first three fractions, which contain comparable amounts of units derived from the optically active comonomer M_1, have optical rotation of the same sign as the homopolymers of M_1, whereas the last fraction, which contains a much smaller amount of units from M_1, has optical rotation of the opposite sign (Table V).

The only possible explanation of the inversion of the optical rotation sign is that the last fraction is mainly formed by macromolecules predominantly originated from the antipode of the racemic monomer M_2 having opposite optical roation with respect to M_1. The previously extracted fractions should, therefore, mainly contain copolymer macromolecules originated from M_1 and the other antipode of M_2, thus confirming the stereoselectivity.

For instance, in the case of the copolymerization of racemic 1-methylpropyl vinyl ether with (*R*)-1-phenylethyl vinyl ether the process can be represented, to a first approximation, as in Scheme I. Obviously the reaction reported in Scheme I is not the only one taking place, but it occurs to a larger extent than that expected on a statistical basis.

SCHEME I



A quantitative evaluation of the stereoselectivity is at present not possible since the efficiency of solvent extraction in separating copolymer from homopolymer is not known, but, in any case, is certainly not very high.[4]

Conclusions

The results obtained in the present investigation unequivocally demonstrate that the copolymerization of a racemic vinyl ether with an optically active one, both bearing an asymmetric carbon atom directly bound to oxygen atom, can be stereoelective and stereoselective when heterogeneous stereospecific catalysts are used, in spite of the absence of transition metals in the catalytic complex.

With regard to the mechanism leading to the above steric features of the polymerization, it is interesting to note that: (a) the antipode of the racemic monomer which is polymerized at a higher rate is that which gives rise to copolymer macromolecules with the optically active comonomer, even if the latter has a lower reactivity with respect to the former; (b) no simple relationship exists between absolute configuration of the optically active comonomer and of the antipode of the racemic comonomer polymerized with the higher overall rate; (c) homogeneous catalytic systems [$BF_3 \cdot O(C_2H_5)_2$] do not seem to be stereoselective.

Considering these results, it seems likely that the induction by the growing chain end is not the only factor responsible for the configuration of the next inserted monomer molecule, but that the catalytic complex, perhaps including a complexed or reacted monomer molecule,[17] can also play an appreciable role.

Work is in progress to establish whether stereoselectivity and stereoelectivity are dependent on the racemic and optically active monomer structure as well as on the nature of the catalyst and on the ratio (R_m) of the racemic monomer to the optically active one.

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Poly(2,6-diaryl-1,4-phenylene oxides)

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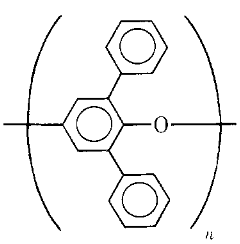
ABSTRACT: Some 2-aryl-6-phenylphenols have been synthesized by a variety of routes. Several phenols have been prepared by reaction of various substituted cyclohexanones with the Grignard reagent prepared from 2-chloro-6-phenylanisole followed by dehydrogenation and demethylation. The most general route identified is *via* condensation of acrolein with substituted dibenzyl ketones followed by dehydrogenation. High molecular weight polymers have been prepared by oxidative coupling only from phenols which do not have substituents in the *ortho* position of the pendant aryl group.

A recent publication[1] described the successful oxidative polymerization of 2,6-diphenylphenol (I) to a high molecular weight aromatic polyether, poly(2,6-diphenyl-1,4-phenylene oxide) (II). A search of the literature failed to disclose other syntheses of



II

2,6-diarylphenols without substituents in the other positions, and the synthesis of a number of such compounds by a variety of methods as well as their polymerization is the subject of the present paper.

A. Plesek[2] self-condensed cyclohexanone in the presence of sodium hydroxide to a mixture of cyclohexanone trimers which, as a structure proof, were converted to 2,6-diphenylphenol by a dehydrogenation reaction.

B. Treatment of 2-phenoxybiphenyl with phenylsodium yields 2,6-diphenylphenol as a product. Minor amounts of 2,6-diphenylphenol were also obtained from diphenyl ether and phenylsodium.[3] In addition, the compound has been observed as a by-product in the related commercial synthesis of phenol from chlorobenzene by treatment with aqueous alkali at elevated temperatures.[4]

C. The synthesis of 2,6-diphenyl-4-nitrophenol from nitromalonaldehyde and dibenzyl ketone was first described by Hill[5] and has been used by Luttringhaus[6] and Oki[7] as an intermediate in the synthesis of 2,6-diphenylphenol.

D. Betts and Davey[8] have also prepared 2,6-diphenylphenol by a sequence of reactions starting with the condensation of malonic ester with 2,4-diphenyl-3-oxobutyltrimethylammonium iodide which yields the intermediate 2,6-diphenyl-1,3-cyclohexanedione.

Results and Discussion

I. Synthesis of Phenols. None of these routes has been found to be readily adaptable as a general synthesis for 2,6-diarylphenols; hence a number of other routes were examined as follows.

E. Phenol or *o*-phenylphenol can be alkylated with cyclohexene to yield 2,6-dicyclohexylphenol or 2-cyclohexyl-6-phenylphenol, respectively,[9] both of which can be dehydrogenated to 2,6-diphenylphenol. Since appropriately substituted cyclohexenes are not readily available and the alkylation with substituted cyclohexenes would yield isomers, no other diarylphenols were synthesized by this route.

The self-condensation of cyclohexanone (method A) has been extended to 2-cyclohexylcyclohexanone. Subsequent dehydrogenation of the dimeric product gave a low yield of 2-(2-biphenylyl)-6-phenylphenol (IVd). Similarly from 2-methylcyclohexanone we have prepared 2-methyl-6-*o*-tolylphenol (V).

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